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REMOTE SENSING

Environmental Effects of Surface Films
Final Report

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1.0 BACKGROUND

This report describes a portion of a program involving both experimental and theoretical studies of the influences of natural biogenic sea surface films on air-sea interfacial parameters. In addition, the role of physical processes in the marine environment on the film's state and transport was investigated. Initial objectives included the determination of the effects of (1) currents on film formation and intensity, (2) surface films on waves, (3) surface films on wave/current interactions, and (4) surface films on near-surface turbulence. During the planning phase of the program these objectives were refined to emphasize the following specific subject areas:

(1) Film transport and modulation by currents

(2) Surface-film influences on capillary waves for surface film concentrations and strain rates appropriate to surface effects of ocean internal waves.

(3) Determination of the effect of surface films on the wind-wave relaxation rate (beta) by direct measurement at wavelengths of interest to microwave radar imaging.

2.0 REVIEW OF PROGRAM ACTIVITIES

ORINCON Principal Investigator W.D. Garrett, has performed several functions within this program, including ongoing consultation with the program manager. In the initial stages of the program, a three-day workshop was organized to review the knowledge base and develop a tentative multi-year research and assessment program. Prior to the workshop; issues, objectives and tentative approaches were developed to formulate a base for the experimental/theoretical program. Considerations included model development, tank studies, and coordinated multidisciplinary field experiments. As technical advisor to the program manager, advice was provided on workshop and program participants. The workshop report was refined through numerous iterations and consultation was provided on the prioritization of the proposed tasks.

2.1 A document has been prepared which addresses surface film deployment and measurement strategies and surface film selection criteria. This report includes specific recommendations on choices of (1) a physical model surface film; (2) a chemical model film and (3) techniques for the collection of natural organic sea-surface, film-forming material for use in laboratory tank studies. This information is incorporated into this final report.

2.2   A 07 DEC 88 meeting was held with program participants at TRW, Los Angeles, to (1) prioritize experiments, (2) discuss measurement methodologies, and (3) review the chemical (organic surface film) aspects of the experimental program. These considerations were subsequently discussed with the program manager on 21 DEC 88, at which time the sequence and nature of the experimental/modeling efforts were reviewed in detail. A presentation was made on surface film issues which was based upon research and analysis performed within the last several months. Surface film selection criteria were developed, taking into account a number of factors including visceolastic parameters, chemical structures, and the nature of the planned laboratory experiments. Three organic films were identified as physical models of natural films, and natural sea water was found to be an appropriate film-forming medium for one of the principal experiments.

2.3   The possible use of an at-sea bubble generator for the concentration of natural surface-active organic material was evaluated within this reporting period. However, the quantity of active organic material collected by this device was not sufficiently large for use in the planned laboratory experiments. The three acceptable model ocean-film chemicals were acquired and delivered to the TRW laboratory facility for use in the planned experiments. Film deployment strategies and measurement methodologies were recommended for the determination of film motion, surface tension, and surface elasticity.

2.4   Three appropriate material were selected, acquired, and delivered to TRW, Redondo Beach, CA, where tank experimentation was performed. A surface marking substance was also proposed. Recommendations for experimental strategies were developed which included types of surface films to be used and their methods of deployment and manipulation on experimental water surfaces. Selection of a specific film-forming material or natural seawater film was determined by the nature of the oceanic process being studied and the characteristics of the experimental facilities. During several periods, ORINCON Principal Investigator W.D. Garrett, worked at the TRW research tank facility to integrate the surface films into the various experimental schemes. Work included, (1) the production of spreading solutions capable of yielding appropriately low surface concentration of surfactants, (2) demonstrating film deployment techniques, and (3) participating in calibrations of a surface tension/elasticity sensor to be used in film effects studies. Film pressure vs. area curves were prepared from a quadratic equation based on experimental data. These curves were used to

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determine the quantity of material required to produce specific surface concentrations and film conditions.

2.5   On 2 July 89, these activities were reviewed for the program manager and for a review group of scientific experts (Jason Group) in San Diego, CA. During the period June to September 89, consultation was provided to the TRW research team studying (1) film transport and modulation by currents, and (2) organic film influences on capillary waves as a function of surface density and strain rates in tank studies of the surface effects of internal waves. Plans were discussed and formulated for out-year laboratory tank studies involving organic surface films.

3.0   SELECTION CRITERIA

The primary criterion for the selection of organic surface films for wind-wave tank research in this program is that the experimental films resemble natural organic slicks as closely as possible. Ideally, the chosen film should match those in the real world in both chemical constitution, rheological properties, and most importantly, the film effects on air-sea interfacial parameters and processes. In experiments involving controlled environment tanks, it might be feasible to import freshly-collected sea-water to achieve the most realistic surface film conditions. Seawater will be recommended for certain experiments in this program, and the special water surface manipulations required will be addressed in a subsequent section.

Present technology in marine microlayer sampling and characterization does not allow for either the collection or synthesis of a truly natural film for laboratory experimentation. However, three model film approaches are recommended in order to approximate a natural sea-surface film as closely as possible. These include (1) a model film based on visco-elastic properties, (2) a model film formulated to duplicate the chemical constitution of natural organic slicks, and (3) natural film-forming substances concentrated and collected by a bubble-scavenging system which can be operated at sea.

4.0   CLASSES OF EXPERIMENTAL SURFACE FILMS

4.1   The Physical-Model Film

Film pressure vs. area isotherms have been measured on natural films collected by surface-microlayer samplers (Barger, Daniel, and Garrett, 1974). Barger (1985) has

compared numerous film pressure area plots for film on natural waters with those of chemically known, surface-active agents, in order to derive knowledge of the hydrophil-lipophil (HLB) balance of the natural films. Several commercially available surface active compounds formed films that exhibited strong similarities in their visco-elastic properties with films formed on natural seawater. Of these PEG 200 monolaurate is readily available and was recommended for study. Obviously this physical model film is a synthetically produced material and does not resemble the natural condition in a chemical sense. However, this physical-model film mimics visco-elasticity and the HLB of natural films as films as well as their particle solubility characteristics. Since these physical considerations determine the influence of the film on the physics of the air-water interface, PEG 200 monolaurate was included in film-effects research. In addition, oleyl alcohol and triolein are recommended as being similar but not identical to the surface physics of natural films. Furthermore there is large quantity of scientific literature devoted to at-sea studies of the effects of monomolecular film of oleyl alcohol on sea surface physics and remotely sensed imagery.

4.2 The Chemical Model Film

Sea surface microlayer collections have been chemically analyzed by several investigators. The composition of natural films is spatially and temporally variable and depends upon numerous physical and biological conditions in the marine environment. In addition, the chemical constitution is extremely complex, representing the many classes of material produced biogenically in the sea. Williams et al. (1986) has attempted to measure the principal chemical classes present in microlayer collections (proteins, lipids, carbohydrates, etc.). Even in this comprehensive study, approximately 60% of the organic film-forming material remained uncharacterized.

On the basis of the research of Williams et al. (1986), the following formulation approximates the chemical constitution of natural film-forming material.

- Protein: heptone from soybeans, C/N approx. 6

- Carbohydrates: alginic acid, MW-240,00   (polymannuronic acid)

- Lipid: triolein, MW=885.4

Mix peptone (25% as carbon), alginic acid (50% as carbon), and triolein (25% as carbon). It should be restated that these three components account for only 40% of the total carbon in a natural film. The remaining 60% is almost completely unknown chemically.

The visco-elastic properties of such a mixture have not been determined. Consequently, it is not clear whether this chemical-model film would be of value in studies of film effects on air-sea interfacial properties. On the other hand, this film would have more realistic solubility characteristics than the physical-model film. That is, the more soluble constituents would be excluded from the water surface during straining and compressional events which stress the film. Should the chemical-model film be formulated for use in tank research, its rheological properties must be determined under controlled conditions in a hydrophil balance for comparison with those of natural sea surface material. Because of the unlikely possibility of duplicating the physics of natural films with a chemical model film mixture, this approach was not recommended.

4.3 Bubble-Collected Natural Film-Forming Material

A cylindrical device has been developed and patented (Van Ry, 1987) which generates surfactant-scavenging bubbles in the sea. The resulting foam-water-particle mixture is collected by overflow at the top of the bubble-scavenged water column. The system, available from MAC Industries Inc., Annapolis, MD has been designed to concentrate the resulting foam and reduce the collected quantity of bulk water. This "slick" sampler-bubble generator was evaluated as a possible tool to acquire natural film-forming organic material from the sea. If it is feasible to collect sufficient material for tank studies, the resulting material would produce films that are quite realistic, and embody the parameters of both the chemical and physical-model slicks. Furthermore, natural derived films may provide the only means of adequately studying the problem of surface scar persistence.

It is recognized that this device exaggerates one of the mechanisms by which biogenic slicks are formed. The vigorous bubbling may also lyse marine organisms in a less than natural manner. Organic containing particles and some chemical classes might be collected with concentrations exaggerated over those associated with a more naturally generated surface film.

However, in spite of these shortcomings, this collection device may produce the most realistic oceanic film possible for tank studies. An evaluation of this device in May 1988, included an assessment of its ability to collect and concentrate film-forming organics in the foam-particle mixture produced by the floating bubble collector. The collected bubble-scavenged organics were spread into a hydrophil balance for film pressure vs. area characterizations of the resulting surface films. The area of the film formed from a specific volume of bubble-collected material was determined so that collection quantities required for experimental tank coverage could be calculated.

It was determined that one ml of collected foam liquid produced 1.07 square centimeter of film when spread into a water surface at film pressure of 5 mN per meter. Thus, 9.3 liters of foam concentrate would be required to cover one square meter of water surface with a monomolecular film. Since the experimental tanks used in this research have 10-20 square meters of surface areas, exhorbitant quantities of foam mixture would have to be collected and transported. Furthermore, spreading of such large quantities of foam mixture onto the experimental tank surface would be extremely slow and tedious with no guarantee that a successful film could be maintained for the time periods required for an experiment.

4.4 Films From Natural SeaWater

Natural seawater is difficult to collect, transport, and store. However, it represents a source of realistic films, and may be appropriate for certain experiments in low-volume tanks. When it is possible to use freshly collected seawater, the following procedures should be followed to handle the films formed from the natural organic surface-active substances present. Seawater is added to the tank and allowed to come to an equilibrium state with regard to turbulence, temperature, entrained air bubbles, etc. During this period of time, an organic film will form at the surface. The surface pressure of this film (a function of the surface concentration of film-forming molecules) will be determined by the organic richness of the seawater and various transport factors. This film can be manipulated for experimentation by the techniques identified in the ensuing section.

A more controlled experiment would be involve cleaning the surface of the film formed during the seawater equilibration, then allowing new film to form gradually by adsorption of film-forming polar molecules. This is a relatively slow process. The transport of polar molecules will be diffusion controlled if there are no other vertical transport processes (bubbles or thermal upwelling) in the experimental tank. The surface properties of the films and the air-water interfacial properties affected by them can be determined as the film develops by adsorption from the bulk seawater substrate.

5.0   SURFACE FILM DEPLOYMENT

Spreading of monomolecular organic films over the surface of a laboratory tank can be readily accomplished even under wind-wave conditions if the film-forming material has the following properties. The surface-active substance should be fluid, spontaneously spreading and autophobic. Autophobicity is a property of relatively pure, surface-active

fluids, where the excess film-forming material does not spread over its own monomolecular layer. Instead, the excess remains in spreading equilibrium with the monolayer as an unspread liquid lens at the monolayer collapse pressure. The unspread excess acts as a reservoir to replace monolayer lost to film-dispersive processes, such as evaporation, dissolution, wind-wave dynamics, etc. Continuous controlled addition of such a material results in a uniform monolayer over a wind-driven tank water surface with the film at its maximum (collapse) pressure.

Film-forming materials which are autophobic include oleyl alcohol (cis isomer of 9-octadecen-1-ol), glycerol trioleate, and PEG (200) monolaurate. The latter compound is the physical-model agent described in the film-selection. section. Oleyl alcohol and glycerol trioleate have been used widely in both tank and field research to demonstrate the physical effects of pure monofilms on air-sea interfacial processes and the resulting modulations of remotely sensed signals. Fluid film-forming chemicals can be dispensed at low, controlled rates, with a syringe pump onto the upwind end of a wind-wave tank,. Dispensing rates for wind-driven experiments can be calculated from the surface concentration required to form a monomolecular layer (1-2 mg/m^2) and the wind-driven surface flow (approximately 3.5% of the wind velocity).

An exact value of the surface concentration for a pure material can be calculated from:

$$mg/m^2 = \frac{MW(mg/mole) \times 10^{20} \ (A^2/m^2)}{(A^2/molecule) \times 6.023 \times 10^{23} \ (molecules/mole)}$$

where the molecular area in square Angstroms (A^2) per molecule corresponds to a point of interest on the surface tension vs. area-per-molecule isotherm.

The rate of dispensing the film forming material (mg/sec) into a fully compacted monolayer is the calculated surface concentration (at equilibrium collapse pressure) in mg/m^2 times the wind-driven surface flow (m/sec) times the width of the tank in meters. This value is the rate required to account for surface renewal caused by the wind-surface coupling.

When no wind is involved or when an experiment requires the use of less than fully compacted monofilm, equation (1) is used to calculate surface concentration. It is possible to perform experiments at surface concentrations below that where water surface parameters are effected, in order to study strain-generated films and their surface effects.

Should it be possible to collect sufficient film-forming material for tank studies with the *in situ* bubble generator (section 1.3), a different form of spreading onto the tank-water

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surface is required. The natural organic surfactants will be part of a bubble-particle-water mixture. This fluid should be allowed to flow at calculated rates down an inclined plane onto water surface. This procedure allows the polar organic surfactants to contact and spread across the water surface in the experimental tank. The quantity of the mixture and its rate of dispensing will depend upon the contained concentration of film-active material as determined by hydrophil balance studies.

In addition to film-deployment techniques, film manipulation and removal procedures are required. A clean water surface is essential prior to the addition of known surface film. The simplest cleaning procedure uses wind to drive the largely water-insoluble film to the down-wind end of the tank. Removal by overflow is most effective when it is possible to raise the tank water to the required elevation. Otherwise, vacuum skimming in conjunction with wind is effective in film removal. Floating power (clean talc or PTFE powder) can be added to the residual film to indicate the progress of the removal process. Films may be manipulated on the water surface by movable hydrophobic surface barriers. These may be solid bars or floating waxed cords. The type of surface barrier used depends upon the tank design and the nature of the experiment.

6.0   SURFACE PROPERTY MEASUREMENTS

Measurements techniques for tank water surface properties vary from long-used existing methods to sophisticated systems under development for the Office of Naval Research (ONR) initiative on Marine Microlayer Processes. The latter suite of measurement systems may someday allow for the continuous in *situ* measurement of capillary wave attenuation, surface tension, and visco-elastic properties of surface films. At the present time, the accuracy and efficiency of the devices has not been proved.

Existing methods for surface tension measurements are outlined in the *Program Workshop Report*, Systems Planning and Analysis Inc., Feb 1987. For calm water tank experiments, the Wilhelmy Plate method can provide continuous surface tension measurement at a specifi. point in the tank. A platinum plate suspended in the surface is attached to a calibrated strain gage or torsion wire. For a less stable, wavy surface, the calibrated spreading oil method (Garrett and Duce, 1980) provides a mobile, but not continuous method of surface tension determination. When used in small quantities, the oils added to the water surface should not modify the experimental results. These oils are

not water soluble and will be removed during surface cleaning procedures between experiments.

7.0   APPLICATIONS TO OTHER PROGRAM ACTIVITIES

During the latter years of this contract various activities were pursued in support of the Spangle Program and other related activities of the Program Office. The Principal Investigator, William D. Garrett, was also involved in an ONR Accelerated Research Initiative on Marine Microlayer Processes, a program studying the basic role of organic films on air-sea interfacial processes and developing new film measurement technologies. Consequently, he was requested by the Spangle Program Manager to present information on sea surface film measurement methodologies to NA-17 planning meetings in preparation for coordinated at-sea studies.

These presentations were made on 3 July and 2-3 November, 1989 and on 9-10 January 1990. Detailed information was supplied to the NA-17 Program Manager and to the planning group on the capabilities within the scientific community for the measurement of sea surface film parameters. The reviewed techniques included (a) measurement of sea surface tension using the calibrated spreading oil method as incorporated in the Surface Tension Measurement System developed at the Naval Research Laboratory, and (b) determination of the levels of surface-active organic substances in near-surface waters using the Self-Contained Underway Microlayer Sampler (SCUMS) develop for and utilized in the ONR Marine Microlayer Processes ARI.

The SCUMS multi-sensor system is mounted on a towed catamaran and measured the following surfactant and oceanographic parameters; the slope spectra of capillary and short-gravity waves with a laser slope gauge, dissolved organic materials using UV absorbance, and the viscocity of the sampled layer using an induction viscometer. Simultaneously, real-time measurements of near-surface temperature, velocity and turbulence were also provided by the SCUMS multi-sensor catamaran system.

Two reports were performed for the Program Office for application to present and future research needs related to the remote sensing of sea surface phenomena involving organic sea surface films. The report of 10 September 1990, is entitled "Involvement of Organic Sea Surface films in the Highlighting of Surface and Underwater Oceanic Processes in Remotely Sensed Imagery". This report emphasized the Problem of Sea Surface Film

Persistence. The second report, prepared in September of 1991 is entitled "Additive Sea Surface Films for use in Non acoustic ASW Field Experiments". These technical reports prepared under this project are included as Appendix A and Appendix B respectively

8.0   BIBLIOGRAPHY

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Williams, P.M., A.F. Carlucci, S.M. Henrichs, E.S. Van Vleet, and K.J. Robertson (1985), "Chemical and microbiological studies of sea-surface films in the southern Gulf of California and off the west coast of Baja California, "*Marine Chemistry* 19, pp. 17-98.

PEG (200) MONOLAURATE
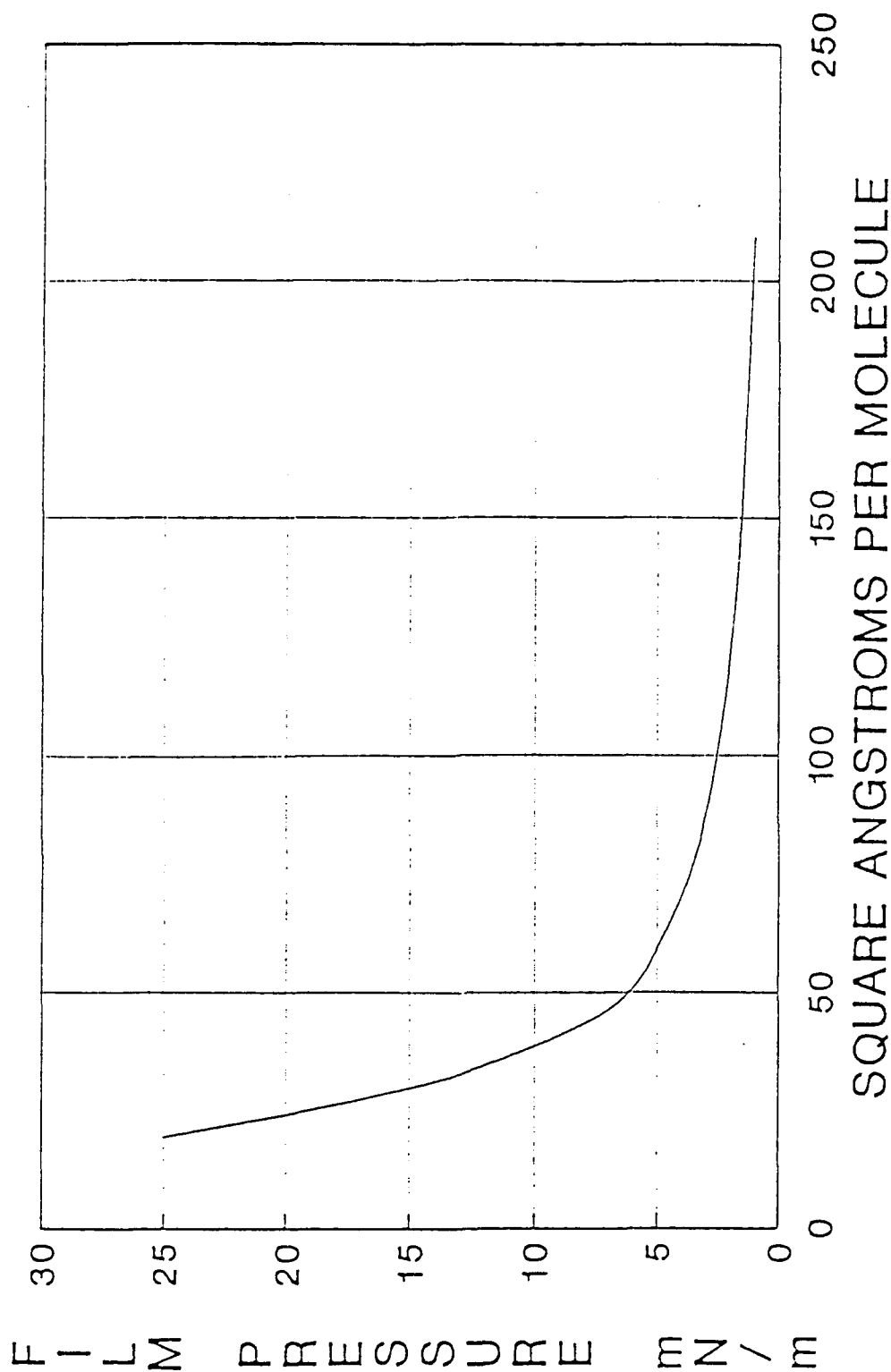
Figure 1. Film pressure vs. area isotherm of PEG (200) monolaurate at 25°C. PEG (200) represents polyethylene glycol groups in the molecule with an average molecular weight of 200.

Plot based on $A = 185/F + 25.1 - 0.52F$
Molecular weight = 3.993×10^5 mg/mole
Specific gravity = 0.984 @ 25 degrees C

OLEYL ALCOHOL
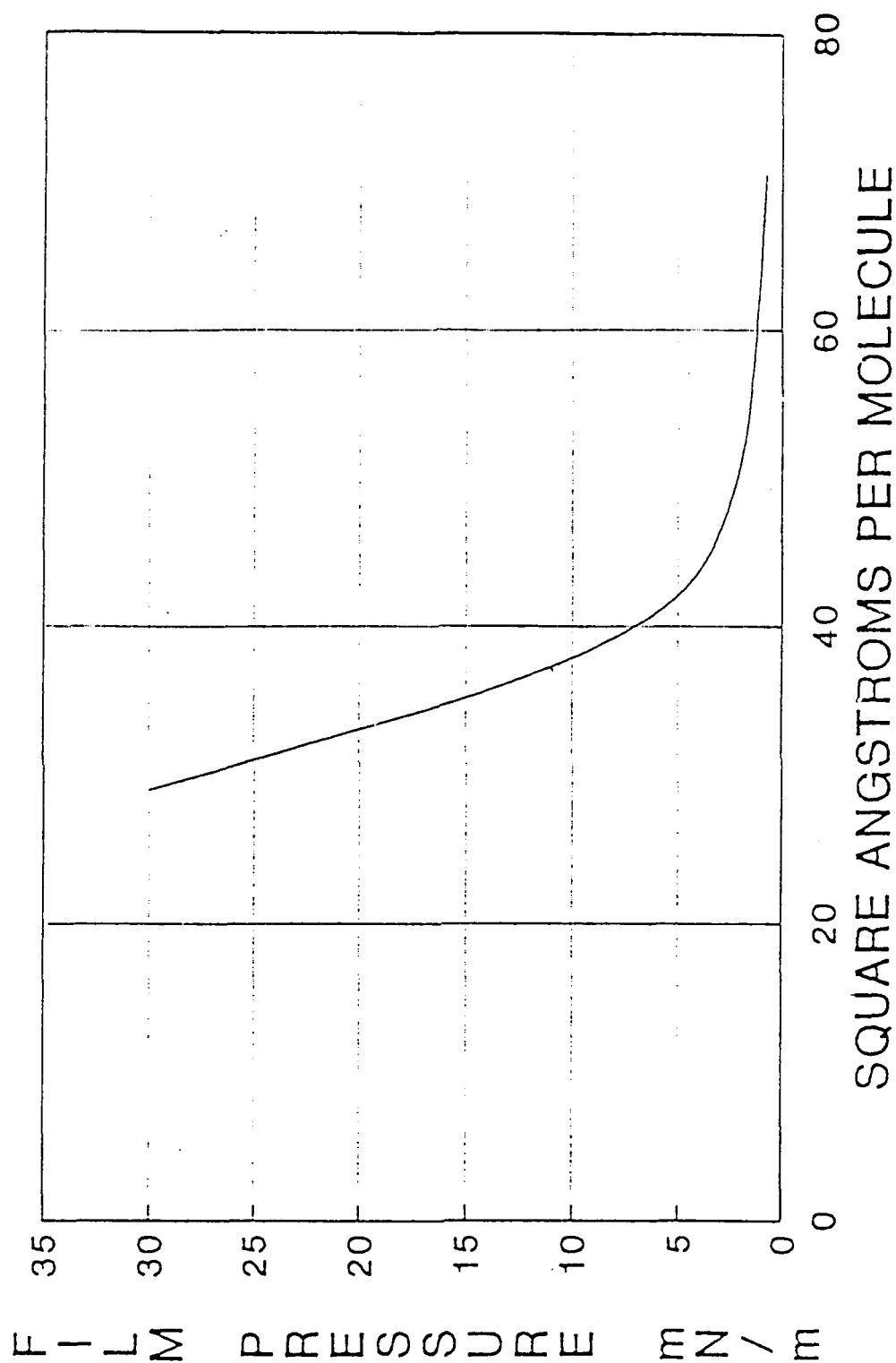
Figure 2. Film pressure vs. area isotherm of oleyl alcohol (cis isomer of 9-octadecen-1-ol) at 25 degrees C.

Plot based on $A = 23.9/F + 38.9 - 0.35F$
Molecular weight = 2.685 x 10^5 mg/mole
Specific gravity = 0.85 @ 25 degrees C

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GLYCERYL TRIOLEATE
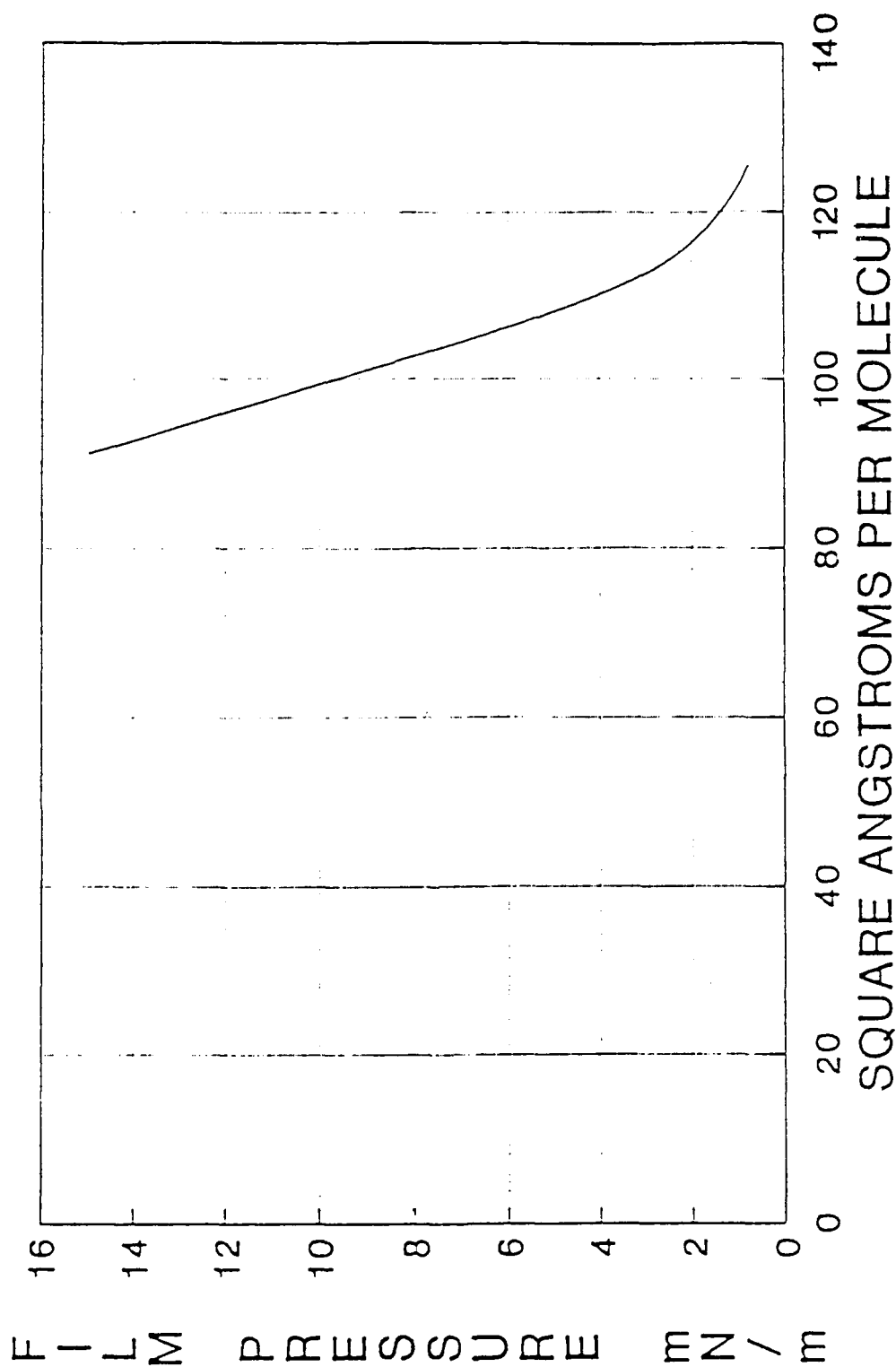
Figure 3. Film pressure vs. area isotherm of glyceryl trioleate (triolein) at 25 degrees C.
Plot based on $A = 9.61/F^2 + 114 - 1.57F$
Molecular weight = 8.855×10^5 mg/mole
Specific gravity = 0.916 @ 25 degrees C

PRESSURE VS . AREA ISOTHERM

FILM PRESSURE mN/m

SQUARE ANGSTROMS PER MOLECULE

—— PEG (200)   ······· TRIOLEIN   —— OLEYL
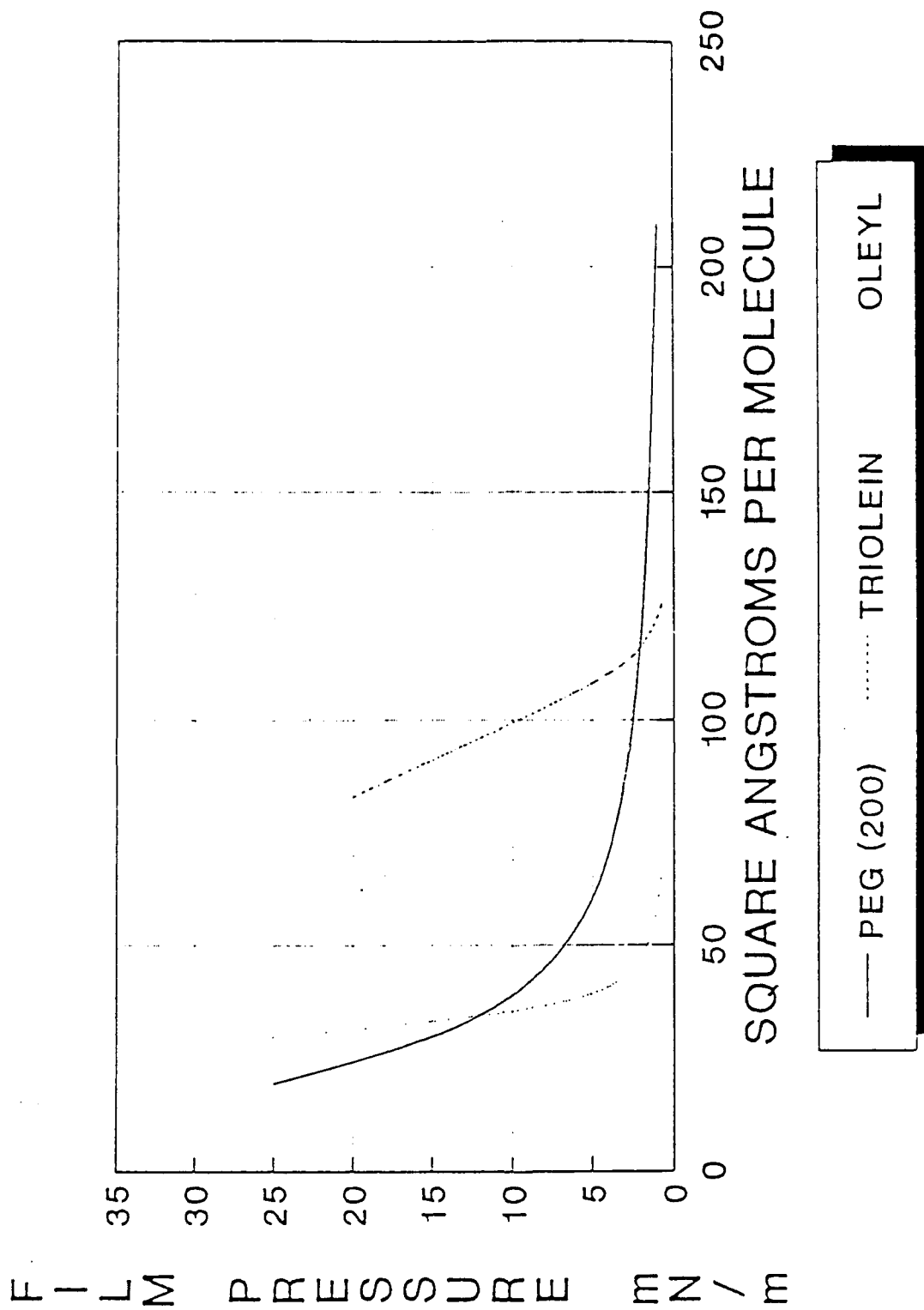
Figure 4.   Composite film pressure vs. area isotherms (25°C) for the film-forming chemicals graphed separately in Figs. 1-3.

SURFACE FILM SELECTION

- CHEMICAL MODEL

- PHYSICAL MODEL

- NATURAL
  - AIR BUBBLE COLLECTOR
  - SEAWATER

Figure 5. Types of surface films considered in this project for use in experimental tank research on film-environment interactions.

Figure 6. Types of surface films recommended for various proposed tank experiments. Model film refers to the physical-model, film-forming substances plotted in Figs. 1-4 and named in Fig. 3.

MODEL FILMS-PHYSICAL

- ● POLYETHYLENE GLYCOL (200) MONOLAURATE

- ● GLYCERYL TRIOLEATE

- ● OLEYL ALCOHOL
  9-OCTADECEN-1-OL (CIS)

Figure 7. Physical-model films recommended for use in tank experiments on surface film-environmental interactions.

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APPENDIX A

ADDITIVE SEA SURFACE FILMS

for use in

NON-ACOUSTIC ASW FIELD EXPERIMENTS

Compilation of Information on
Materials and Methods

Technical Report
September, 1991

Prepared By

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ADDITIVE MONOMOLECULAR FILMS AS INDICATORS OF SEA SURFACE AND UNDERWATER PROCESSES

It is possible to generate artificial organic films on the
sea surface or to introduce sub-critical levels of film-
forming substances to act as remotely sensible indicators of
surface and underwater oceanic processes. This approach is
especially valuable when the sea surface concentration of
natural film-forming materials is low and no natural sea
slicks exist, or when air-sea dynamics preclude the
existence of natural films. Certain additive surface films
have been shown to be persistent and readily detectable in
winds as great as 10 meters per second. Relevant
publications and supporting graphics are included in this
document. Such films can be used to determine currents
across shear boundaries, surface flow (a resultant of wind
drift and current vectors), and as an approximate model to
mimic natural films for research purposes.

Sub-critical concentrations (less then approximately 1 mg
per square meter) are levels of film-forming material below
which no coherent film will form. At these low surface
concentration levels remotely sensible air-sea interfacial
processes are not altered. However, if the sea surface has
been seeded with surface-active organic material to levels
just below that where a detectable film will form,

convergences due to Langmuir circulation, internal waves, upwellings etc., could increase the surface concentration of the additive surfactant to a point where a sensible sea surface film would result. The quantities of surface-active material required to seed the sea surface are readily calculated from hydrophil balance data (film pressure or wave damping vs film area curves). Air and ship dispensing procedures are available, and there are potential controlled-release techniques which can be developed for the production of a controlled surface concentration of indicator-film material.

Applications of additive surface films at various surface concentration levels are summarized in the accompanying graphics. When natural films do not exist, the artificial slicks may be used to (1) highlight sea surface processes, (2) simulate surface film effects for studies of film influences on remotely sensed imagery, and (3) indicate surface manifestations of underwater processes. All active and passive remotely sensed signals are influenced by sea surface films. The processes modified by the films affect the sensor signal. The character of the film-effect/sensor-response relationship is determined by the sensor type and spectral range. Consequently, additive indicator films have application to a broad range of sensors, including SAR, RAR, thermal IR, and microwave radiometry [Garrett and Barger, 1980].

SELECTION CRITERIA FOR SEA-SURFACE FILM-FORMING MATERIAL

Criteria for the selection of materials for the generation
of a sea surface film depends upon the particular Naval or
civilian application involved. Considerations include:

    1. desired film persistence
    2. interfacial parameters to be modified; e.g.
capillary waves, surface bubble and foam stability, surface
temperature, etc.
    3. optimum film geometries
    4. deployment requirements
    5. environmental conditions in area of application;
winds, sea state, air-sea stability, sea temperature, etc.

Once these requirements have been identified, film-forming
substances can be selected on the basis of a suite of
chemical and physical properties which will satisfy the
particular application. The properties of both the bulk
chemical and its spread film must be considered. The
physical and chemical properties are determined by the
structural and chemical characteristics of the film-forming
molecule, its chemical functional groups, and even its
geometric shape.

Film-forming agents are surface-active, composed of polar
organic molecules which adsorb at a phase boundary, reduce
its surface free energy, and modify its viscoelastic
properties. Oceanic phase boundaries of interest include
the air-sea interface, the air-water interfaces of air
bubbles and foam at the sea surface, and the surfaces of
bubbles and particulate matter in the bulk ocean. Within

the chemical industry there are thousands of off-the-shelf
surface-active chemicals exhibiting a broad range of
physicochemical properties. Many of these can be used to
form spread or adsorbed films at interfaces in the marine
environment.

SELECTION CRITERIA FOR A REMOTE SENSING STUDY

An example of criteria for selection of a persistent and
continuous sea surface film are described in the enclosed
publications [Garrett and Barger, 1980; Hühnerfuss and
Garrett, 1981]. Simulated sea slicks were utilized in the
MARSEN (Marine Remote Sensing) Experiment to demonstrate
slick effects on both active and passive remote sensors.
Table 1 lists property requirements for both the film-
forming agent and its spread film.

Table 1

PROPERTIES REQUIRED FOR THE PRODUCTION OF SIMULATED SEA SLICKS IN THE MARSEN EXPERIMENT

MONOMOLECULAR - SMALL QUANTITIES COVER LARGE AREA
AUTOPHOBIC - FILM IN EQUILIBRIUM WITH BULK LIQUID
STRONG SURFACE EFFECTS - SIGNIFICANT WAVE ATTENUATION
                         - RESISTS WAVE FORMATION
                         - IMMOBILIZES SEA SURFACE
NONVOLATILE - LOW EVAPORATIVE LOSS RATE
NONIONIC - LITTLE REACTION WITH SALINE WATER
LOW SOLUBILITY - FILM PERSISTENCE
FLUID FILM - RAPID, SPONTANEOUS SPREADING
           - HIGH RESPREADING POTENTIAL
LOW FREEZING PT. - EFFECTIVE FLUID FILM IN COLD SEAS
NONTOXIC - ECOLOGICALLY ACCEPTABLE

To achieve this suite of properties it is necessary to consider the molecular constitution of the film-forming material and its relation to the physicochemical properties of the agent and its spread film. The molecule of the slick-forming material should contain a hydrophilic group which adsorbs at the water surface and a hydrophobic hydrocarbon chain which is oriented away from the water surface when the film is under lateral surface pressure. The agent must spread spontaneously over the water surface as a water-insoluble monomolecular film, so that only small quantities are required to affect a large water surface area. The hydrocarbon portion of the molecule should contain 16-18 carbon atoms or more, so that losses from the slick due to evaporation and dissolution will be small. A nonionic, film-forming chemical is required for use on sea water to obviate reaction with ionic species which would increase film solubility.

Compounds of the type described in this section, if relatively pure, spread spontaneously across the sea surface into monomolecular films. Because there are losses from the film due to peripheral spreading at the slick edges and dispersion of the film material out of the surface by air-sea dynamics, an excess of film-forming material is dispensed to replace lost film and maintain its lifetime. These film-forming chemicals possess a property called

"autophobicity", i.e. the excess liquid does not spread over its own monomolecular film, but remains on the surface as bulk droplets in equilibrium with the film. Thus, the excess droplets represent a reservoir of material to spread and replace losses of the additive film caused by environmental dispersive processes. Since the film spreading process occur at the sea surface, it is also essential that the film-forming liquid have a specific gravity that is less than that of seawater. It must remain at the sea surface in equilibrium with its film.

Molecular geometry plays an important role in the selection process. It is desirable to dispense fluids and to produce films that are fluid in character. Film-forming materials which are fluid at room temperature and the surface films which they produce have rapid spontaneous spreading. In addition, the films have a high respreading potential into surface areas where the film has been displaced by air-sea interfacial disturbances. It should be noted that the spreading of solid surface-active substances is orders of magnitude slower than for liquid agents.

A nonlinear or bent molecular structure leads to a fluid condition, both in the bulk material and in the spread film. Linear molecules have strong intermolecular forces, are more solid in character for a particular molecular weight, produce films that are slow to spread, and do not respond

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readily to surface perturbations. This problem is overcome by selecting molecules with hydrocarbon chains which are permanently bent or are branched, a condition which prevents the close packing of the hydrocarbon chains in the spread film and allows for fluidity. Alkyl groups which interfere with hydrocarbon chain adlineation include those with a point of chemical unsaturation (cis geometric isomers) yielding a permanently bent chain (e.g. oleyl alcohol), or those with chain branching such as is found in isostearyl alcohol. A relatively new product line of commercially available beta-branched alkanols has become available. These liquids have freezing points well below that of seawater, and may have potential utility in oceanographic programs and applications. However, at present there is little at-sea experience with this class of compounds.

Two liquids were selected to meet the surface film requirements of the MARSEN Experiment, oleyl alcohol (9-octadecen-1-ol, cis isomer) and methyl oleate, the methyl ester of oleic acid. The former is a highly surface-active material which was selected because of its intense damping of microwave scatterers. The methyl oleate has a moderate spreading pressure of 15 mN/m, and was studied because its film pressure was lower and more like that of natural slicks. Butyl stearate (octadecanoic acid, n-butyl ester), with a film pressure of approximately 11 mN/m may, be an even more realistic simulant for natural slicks. However,

little information is available on its surface chemistry, and experience in spreading it as a film onto the sea is essential before it can be recommended.

This report addresses the use of additive organic films in remote sensing exercises such as MARSEN, HIGH RES ONE, and non-acoustic ASW field experiments, where persistent films are desired. There are several other Navy applications for intentionally added organic films at sea which require a different set of properties (foam destabilization, short persistence, etc.) These applications are noted in the presentation graphic entitled "Marine Applications of Artificial Slicks". A discussion of the selection criteria applicable to these other applications will be detailed in future reports to appropriate agencies.

NON-ACOUSTIC ASW STUDIES
ADDITIVE ORGANIC SURFACE FILMS

WHEN NATURAL FILMS ARE NOT ABUNDANT

(1) DEPLOYED AS VISIBLE SLICKS IN VARIOUS GEOMETRIES

(2) FILM CONSTITUENTS DISPENSED IN SUB-CRITICAL
CONCENTRATIONS

TO ELUCIDATE:

SURFACE FLOW
CONVERGENCE PATTERNS
FILM INFLUENCE ON REMOTELY SENSIBLE SEA
SURFACE PARAMETERS

ORINCON CORPORATION

MARINE APPLICATIONS OF ARTIFICIAL SLICKS
SEA SURFACE MODIFYING ORGANIC FILMS

- SURFACE FILM INVOLVEMENT IN REMOTELY SENSED IMAGERY
  - ATTENUATION OF RADAR/VISUAL SURFACE SCATTERERS
  - SUPPRESSION OF WHITE WATER
  - SEA SURFACE TEMPERATURE EFFECTS

- INDICATOR OF SURFACE FLOW

- RADAR/VISUAL DETECTABLE SEAMARKER (SEARCH/RESCUE)

- MODIFICATION OF ENTRAINED AIR BUBBLE DISTRIBUTIONS

- SUPPRESSION OF AMBIENT SEA-SURFACE NOISE SOURCES

- OIL SPILL CONTROL

- PERISCOPE WAKE SUPPRESSION

SEA SLICK SIMULATION
AUTOPHOBIC ORGANIC FILMS

- OLEYL ALCOHOL   31 mN/m

- METHYL OLEATE   15 mN/m

- BUTYL STEARATE   11 mN/m

ORINCON CORPORATION

$CH_3(CH_2)_7CH=CH(CH_2)_7CH_2OH$ (CIS ISOMER)

OLEYL ALCOHOL

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOCH_3$$

METHYL OLEATE

$$CH_3(CH_2)_{16}COO(CH_2)_3CH_3$$

BUTYL STEARATE

$$mg/m^2 = \frac{MW(mg/mole) \times 10^{20}(\text{Å}^2/m^2)}{\text{Å}^2/\text{molecule} \times 6.023 \times 10^{23}(\text{molecules/mole})}$$

Surface concentration of monomolecular film constituents (mg/m^2) as a function of molecular weight (MW) and the area occupied (Å^2) per molecule.

Experimental Sea Slicks: Their Practical Applications and Utilization for Basic Studies of Air-Sea Interactions

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INTRODUCTION

Practical applications of organic surface films added to the sea surface date back to ancient times. Aristotle, Plutarch, and Pliny the Elder describe the seaman's practice of calming waves in a storm by pouring oil onto the sea [*Scott,* 1977]. It was also noted that divers released oil beneath the water surface so that it could rise and spread over the sea surface, thereby suppressing the irritating flicker associated with the passage of light through a rippled surface.

From a scientific point of view, Benja. ... .anklin was the first to perform experiments with oils on natural waters. His experiment with a 'teaspoonful of o on Clapham pond in 1773 inspired many investigators to consider sea surface phenomena or to conduct experiments with oil films. This early research has been reviewed by *Giles* [1969], *Giles and Forrester* [1970], and *Scott* [1977]. Franklin's studies with experimental slicks can be regarded as the beginning of surface film chemistry. His speculations on the wave damping influence of oil induced him to perform the first qualitative experiment with artificial sea slicks at Portsmouth (England) in October of 1773. Although the sea was calmed and very few white caps appeared in the oil-covered area, the swell continued through the oiled area to Franklin's great disappointment.

Giles [1969] reviewed the literature published after Franklin's paper and found 17 authors discussing wave damping by oil prior to 1951. But apart from some experiments on wave quelling by John Shields at Peterhead Harbor (Scotland) in 1882, 70 years passed before surface films again became of interest as a tool for the practical modification of air-water interaction processes, when Mansfield and several other authors started their investigations on the retardation of evaporation by monomolecular films (reviewed by *La Mer* [1962]).

The mechanisms of the wave calming phenomenon are not well understood, especially with regard to gravity wave damping. However, some pioneering quantitative research on the open sea has been performed since 1968, which has led to an improved understanding of some of the effects of organic surface films on air-sea interaction processes [*Barger et al.,* 1970; *Mallinger and Mickelson,* 1973; *Hühnerfuss et al.,* 1980]. Furthermore, slick experiments are useful for studies of the drift response of the ocean surface [*Lange and Hühnerfuss,* 1978], the formation of Langmuir cells, the backscattering of radar signals from the ocean surface [*Hühnerfuss et al.,* 1978; *Hühnerfuss et al.,* 1980], and the gas exchange processes across the water surface [*Brockmann et al.,* 1980]. Thus continued re-

search with experimental sea slicks will be necessary in future years to address such problems.

RATIONALE FOR RESEARCH WITH EXPERIMENTAL SLICKS

Surface-active organic material adsorbs at and spreads over the air-water interface. Slicks at sea associated with windrows, internal waves, calm water, and plankton blooms are surface films of polar organic matter at a sufficient concentration to modify physical interfacial properties. In general, sea surface films are monomolecular organic layers, which often exist at surface pressures below those at which the film physically collapses.

Small-scale hydrodynamic and physical processes are modified at low film pressures, at a point in the area compression plot for the film where it undergoes a transition from an expanded gas-like state to a state where it possesses liquid or solid properties. At this transition point, the air-water interface is no longer 'free' but is immobilized by the incompressible film. This effect has been clearly demonstrated by experiments on the capillary wave damping by water-insoluble organic surface films [*Garrett,* 1967a] and measurements of the influence of surface film pressure on water surface temperature and convective processes near the interface [*Jarvis,* 1962].

Adsorbed surface-active material not only attenuates existing capillary waves but also inhibits wave formation [*Keulegan,* 1951; *Van Dorn,* 1953]. According to *Miles* [1967] the addition of a sufficient quantity of a soluble surface-active agent to produce an inextensible film at the air-sea interface can increase the minimum wind velocity necessary to produce waves by almost 1 order of magnitude. While natural sea slicks should in theory withstand winds of this order (12 m/s), their constituents are dispersed at sustained wind speeds of from 5 to 7 m/s and sometimes less. The concentration of surface-active material in the underlying seawater is insufficient to supply and to maintain a coherent surface film under highly dispersive conditions.

On the other hand, artificially produced surface films of water-insoluble organic compounds may possess the wave-inhibiting properties against winds as high as 12 m/s. On several occasions, artificial slicks have been formed and maintained for a period of time when winds were as great as 10 m/s. Even under these adverse conditions, coherent experimental surface films could be maintained as long as excess film forming material was present to repair ruptures in the man-made slick caused by dynamic processes at the air-water boundary.

The various effects of both natural and experimental surface films on air-sea interfacial properties and processes are

TABLE 1.   Impact of Natural and Man-Made Surface Films on the Properties of the Air-Sea Interface

Surface Effect or Process Modification	Type of Organic Surface Film	
	Natural	Experimental[a]
Capillary wave attenuation	Davies and Rideal [1963][b]	Barger et al. [1970][b]
	Ewing [1950][b]	Hühnerfuss et al. [1980][b]
	Garrett [1967a][b]	
	Scott [1972][b]	
Gravity waves	Davies and Rideal [1963][c]	Barger et al. [1970][b]
		Hühnerfuss et al. [1980][b]
Breaking wave inhibition	...[d]	Barger et al. [1970][b]
Gas transport reduction	...[d]	Jarvis et al. [1962][c]
		Brockmann et al. [1980][b]
		Petermann [1976][c]
Oleophilic pollutant accumulation	Hartung and Klinger [1970][b]	...[d]
	Seba and Corcoran [1969][b]	
	Eisenreich et al. [1978][b]	
Foam stability	Garrett [1972][c]	Garrett [1967b][c]
Air bubble bursting	Blanchard and Hoffman [1978][c]	Garrett [1968][c]
	Garrett [1968][c]	Patterson and Spillane [1969][c]
Surface temperature	Clark [1967][b]	Grossman et al. [1969][b]
		Jarvis [1962][c]
		Jarvis et al. [1962][c]
Electromagnetic wave reflection	Beard and Gainer [1970][b]	Barger et al. [1970][b]
	Brown et al. [1976][b]	Hühnerfuss et al. [1978][b]
	Maurer and Edgerton [1975][b]	Hühnerfuss et al. [1980][b]

[a]A continuous, monomolecular film added to water surface for research purposes.
[b]Effect demonstrated by laboratory and field research.
[c]Significant influence of surface film unlikely.
[d]Potential influence, but not proved by experiment.
[e]Demonstrated in laboratory; field studies if any were inconclusive.

reviewed in Table 1. In addition to the previously mentioned capillary wave and surface temperature effects, natural films modify bubble bursting characteristics and sea foam, alter electromagnetic wave reflection by attenuating capillary and small gravity waves, and act as an interfacial organic phase which accumulates oleophilic pollutants. Wave attenuation and ocean surface temperature effects have been studied by using large experimental slicks at sea, while other film-induced modifications of interfacial properties have been demonstrated solely in the laboratory.

Most of the numerous effects of natural slicks (Table 1) may be duplicated by experimental surface films composed of selected pure compounds. These interfacial modifications may be caused by a wide variety of water-insoluble surface films which modify the microscale hydrodynamics and the rheology of the air-sea interface. It will be shown in ensuing sections that experimental sea slicks are useful for fundamental studies of wave-wave and wind-wave interactions and for the evaluations of the effects of sea surface films on the interpretation of remotely sensed signals. In addition, several practical applications of surface films in the marine environment have been developed in recent years.

EXPERIMENTAL APPROACH

Criteria for the Selection of
Slick-Forming Materials

Several physical and chemical criteria must be considered in the selection of a monolayer-forming material for the creation of a durable, continuous, and surface-active experimental sea slick. The molecular structure of the slick-forming material should contain both polar and nonpolar functional groups: a hydrophilic group which adsorbs at the water surface and a hydrophobic hydrocarbon chain which orients away from the water surface when the film is under pressure.

The material must spread spontaneously into a water-insoluble monomolecular film so that only small quantities are required to affect a large water surface area. The hydrocarbon portion of the molecule should contain at least 18 carbon atoms in order that losses from the slick caused by evaporation and by dissolution will be small. A nonionic film-forming chemical is required for use on saline water to obviate reaction with ionic species which increase the solubility rate. Commercially available materials which satisfy these requirements include fatty alcohols and esters, glyceride esters of fatty acids (vegetable and fish oils), and several synthetic surface-active agents. Table 2 is a sample list of properties required for substances which could be used for the production of persistent, highly surface-active experimental slicks on the sea.

Initial experiments were performed in the laboratory and on the Chesapeake Bay to determine (1) the feasibility of creating and of sustaining a monomolecular film on the sea,

TABLE 2.   Properties of Film Forming Materials for the Production of Persistent, Highly Surface Active Experimental Sea Slicks

	Properties
Highly surface active	strong capillary wave damping; resists generation of air-water interfacial disturbances
Liquid	easily and rapidly spread onto water surface
Nonvolatile	low evaporative loss rate
Nonionic	little reaction with saline water to ensure film persistence
Low water solubility	long film persistence
Fluid monomolecular film	rapid, spontaneous spreading; high respreading potential
Low freezing point	effective fluid films in cold environments
Nontoxic	

(2) the resistance of various monolayer-forming materials to natural dispersive forces of wind, waves, bursting bubbles, etc., (3) the most effective monolayer-forming materials for the creation of a durable experimental slick for various applications and research purposes, and (4) the quantities of surface-active material required.

For comparison purposes, a series of experimental slicks of different substances were produced simultaneously from point source applications. The slicks were made from the following film-forming materials:

1. Oleyl alcohol (9-octadecen-1-ol, cis isomer) an 18-carbon. monounsaturated fatty alcohol, equilibrium spreading pressure = 31 dynes/cm.

2. Cottonseed oil, glyceride esters, primarily palmitic C_{16}, oleic $C_{18:1}$, and linoleic $C_{18:2}$, equilibrium spreading pressure = 14 dynes/cm.

3. Oleyl ether containing two oxyethylene groups, equilibrium spreading pressure = 42 dynes/cm.

4. Isostearyl alcohol containing two oxyethylene groups, equilibrium spreading pressure = 44 dynes/cm.

5. Oleic acid (9-octadecenoic acid, cis isomer), equilibrium spreading pressure = 30 dynes/cm.

6. Sorbitan monooleate, equilibrium spreading pressure = 42 dynes/cm.

Since the slicks were deployed at approximately the same time, they were subjected to similar environmental stresses. These studies were performed several times with small quantities (25–150 ml) of film-forming substances so that the slicks could be observed and their dimensions measured during their lifetimes. The relative slick lifetimes and their capillary wave damping intensities were nearly identical for each series of simultaneously produced slicks. These studies were performed under conditions of steady winds (4–7 m/s) with no natural or pollutant slicks in evidence.

During the first 20–30 min, all of the slicks grew equally to a size determined primarily by wind-driven surface water flow. During this period, excess film-forming material in equilibrium with the spread film was sufficient to overcome losses from the slick owing to natural processes. After a period of about 30 min, the more water soluble films (e.g., oleic acid) no longer increased in surface area. The less soluble films continued to increase in area at about equal rates. At a slick lifetime of about 1 hour, three of the moderately soluble slicks, sorbitan monooleate, isostearyl alcohol (2-OE), and oleyl ether (2-OE) disappeared rather suddenly over a short time period of from 5 to 10 min. Their constituents were no longer at a sufficiently high surface concentration to alter capillary waves and other small-scale interfacial dynamic processes. Since these effects modify light reflectance from a slick-covered water surface, the slicks in question were no longer visible. Oleyl alcohol and cottonseed oil are quite water insoluble even in monomolecular layers, and their films persisted about 3 times as long as any of the other films studied. Film lifetime is an important aspect when using experimental slicks for basic and for applied purposes because of the difficulty in maintaining a one-molecule-thick organic layer against natural dispersive processes. Consequently, oleyl alcohol and cottonseed oil are examples of materials with relatively high and moderate film pressures which can be used effectively to produce persistent experimental slicks on bodies of water.

During the simultaneous observations of the adjacent slicks, it was noticed that the capillary wave damping in the low film-pressure slick of cottonseed oil was less intense than for the other experimental films whose film pressures were 30 dynes/cm or greater. More high-frequency wave structure was visible in the cottonseed oil slick, and its light reflectance effects were less pronounced, having the appearance of natural slicks with similarly low film pressures [Garrett, 1967a].

In the laboratory, using mechanically generated waves, most surface films damp capillary waves to approximately the same degree when their film pressures are on the order of a few dynes cm^{-1} [Garrett, 1967a]. However, in the open water studies, the surface films were at their maximum spreading pressures in equilibrium with unspread droplets of film-forming material. The film pressure of the slicks with strong capillary wave effects (greater than 30 dynes cm^{-1}) was more than twice that of the less effective cottonseed oil film (14 dynes cm^{-1}). Thus the resistance of a slick to capillary wave formation is not solely related to its wave-damping characteristics as measured in the laboratory with mechanically generated ripples. It is not yet known which physical parameters of an organic surface film govern its influence on capillary waves at sea. It has been observed, however, that slicks with high film pressures damp water waves and small-scale turbulence more intensely than those of lower equilibrium film pressure.

Because of its long lifetime and strong surface effects, oleyl alcohol has been used for most experimental sea slick studies. In addition, this material meets the criteria listed in Table 2. On the basis of these criteria, cotton seed oil and methyl oleate are suitable for the production of persistent slicks with lower film pressures which more closely simulate natural films in their physical effects on interfacial properties and processes.

Techniques for Generation of Experimental Slicks

Method A: Dispensing film-forming material from a surface vessel. When organic surface active material is placed on a clean water surface in the absence of wind, it spreads spontaneously in all directions. Its initial intrinsic spreading velocity varies between 34 and 40 cm/s for the types of film-forming materials discussed in this report. The spreading velocity is related in part to the equilibrium spreading pressure of the surface active material [Garrett and Barger, 1970]. The spreading velocity decreases rapidly with distance from the source of the film-forming material, decreasing to 10 cm/s or less when the leading edge of the film is 3 m from the point of application. Under the influence of wind, however, the film is moved along with the flow of the surface water (3–4% of the wind velocity), and the excess bulk material which exists as floating lenses also moves with the wind-driven surface water flow. The rate of motion of the downwind edge of the slick is the sum of the surface water flow and the film-spreading velocity at that point. Thus, a point source addition of spreading oils under the influence of wind produces an elongated slick whose dimensions are primarily a function of wind velocity and surface current.

It is also possible to generate a slick by continuous dispensing from a vessel moving in a direction perpendicular to the wind. However, a stripe of slick does not grow uniformly but eventually forms streaks along the downwind edge, probably owing to convergence zones caused by wind-generated cellular water motions. Langmuir cells and internal waves may also produce surface zones of convergence and divergence which will prevent continuous coverage by the experimental slicks.

Thus to produce a large slick for experimental purposes

TABLE 3. Quantities of Oleyl Alcohol Used in the Production of Various Experimental Sea Slicks

Dispensing Mode	Slick Size, km² [a]	Oleyl Alcohol Volume (l)	l km⁻²	Reference
Boat [a]	0.50	13.0	26.0	*Barger et al.* [1970]
Boat [b]	0.70	19.0	27.1	*Mallinger and Mickelson* [1973]
Fixed-wing aircraft [b]	0.52	18.0	34.6	*Barger and Garrett* [1974]
Point Source	0.005	0.1	20	*Barger and Garrett* [1976]
Helicopter [c]	1.5	30.0	20	*Hühnerfuss et al.* [1978]
Monolayer, theoretical	...	...	1.75	...

[a] Maximum area of slick during its lifetime.
[b] Dispensed as a liquid stream from a pressurized container.
[c] Frozen, 80 g chunks dispensed periodically.

iich has a circular or rectangular shape, it is necessary to int' the slick-forming material onto the water surface. That it cannot be simply dispensed from a point source or a igle stripe but must be laid in adjacent bands or in an ex-nding spiral from either a surface vessel [*Barger et al.,* 1970; *allinger and Mickelson,* 1973] or an aircraft [*Barger and Gar-'t,* 1974; *Hühnerfuss et al.,* 1978].

Method B: Generation of slicks by aerial dispensing of frozen ' cubes. Several problems are associated with the produc-n of experimental slicks from a surface vessel. The vessel ay disturb the natural wave and turbulence fields and possi-y emit interfering chemical pollution. In addition, there is a quirement for the production of large slicks several square lometers in area in a relatively short time. Thus an alterna-'e method for the generation of experimental sea slicks has en developed, whereby frozen chunks (oil cubes) of the sur-ce film-forming material are systematically distributed from helicopter [*Hühnerfuss and Lange,* 1975]. During project off 1974 (Kombiniertes Oberflächenfilm projekt) and Jon-'ap 1975 (Joint North Sea Wave Analysis Project) 80-g unks of 96.5% oleyl alcohol (9-octadecen-1-ol, cis isomer) re prepared by freezing the material to 249 K in small pa-r cups. The frozen chunks were transported in large Dewar ntainers for dispensing from the helicopter.

If changing tidal currents prevail during slick-forming oper-ions, it is essential to drop several chunks to produce a mple slick prior to formation of the main experimental sur-ce film. Thus one can observe the spreading characteristics d direction of drift of the sample slick with respect to a ed point, such as an anchored ship or instrumentation pile. is procedure is necessary to assure that the main experi-ntal slick will drift through an array of wave and meteor-gical instruments or through the footprints of sensors being ed in conjunction with the slick research.

The procedure for the generation of a typical experimental ck by helicopter dispensing of frozen oil cubes is summa-ed as follows:

1. Dispensing pattern: 10 parallel rows perpendicular to : wind (about 50 m apart), 80 g chunks of frozen oleyl alco-l every 4 s, total of 320 oil cubes dispensed.
2. Flight altitude: 30 m (minimum altitude to avoid rotor wnwash, depends upon helicopter type).
3. Flight speed: 93 km/h.
4. Wind velocity: 3.5 m/s for this example.
5. Area of developed slick: 1.5 km².
6. Total dispensing time: 30 min (includes time required the individual frozen oil cubes to melt and to spread).

As was mentioned previously, natural forces displace the ck-forming material from the air-sea interface. The rate at

which this occurs is a function of the intensity of the dynamic processes operating on the interfacial film. To maintain a con-tinuously slicked sea surface area, it is necessary to dispense an excess of film-forming material over that required to form a monomolecular film. The excess material does not increase the slick thickness above that of a monolayer, because the film-forming materials selected are autophobic (i.e., they do not spread over their own monomolecular film). Thus the ex-cess material exists as unspread floating drops in equilibrium with the fully compressed slick. When a portion of the slick is dispersed by natural processes, the excess film-forming mate-rial represents a floating reservoir to replace rapidly the lost organic material and to restore the equilibrium pressure of the surface film. The surface concentration (1 km⁻²) used success-fully in various experimental sea slick studies are listed in Table 3. The quantities used can be compared with that re-quired for a single molecular layer of oleyl alcohol, 1.75 l/km².

Figure 1 is an aerial photograph taken from an altitude of 450 m of a 2.3-km² oleyl alcohol experimental slick recently generated for research purposes during the Marsen (maritime remote sensing) exercise, September 1979. The surface film was formed by dispensing 600 80 g blocks of frozen film-form-ing material from a helicopter. The slick was positioned such that it would pass directly across the Nordseeforschungsplatt-form (54°42'33"N, 7°10'7.4"E) in the German Bight. The slick moved at a velocity of 0.7 m s⁻¹ under a 13 kn wind (u_{10} = 6.7 m s⁻¹) from 290°.

REVIEW OF RECENT BASIC RESEARCH USING EXPERIMENTAL SLICKS

During Jonswap 75, several monomolecular oleyl alcohol films of about 1.5 to 3 km² in area were produced by helicop-ter dispensing of the frozen film-forming material. The influ-ence of the film on wave spectra was measured under moder-ate wind conditions (u_{10} = 3.5 to 7.7 m s⁻¹) by conventional wave staffs, a coherent X band microwave scatterometer mounted on a sea-based platform, and in one case the slick area was overflown by a NASA C-130 aircraft carrying a 13.9-GHz pencil-beam scatterometer (AAFE RADSCAT).

A typical example of the wave attenuation characteristics measured by wavestaffs is depicted in Figure 2. Between 3.2 and 16 Hz, the observed wave attenuation was in the range of about 40–60%, with only a slight increase in damping with fre-quency. In addition, because of the large size of the slick, it was possible to make a preliminary judgment on the influence of a surface film on long gravity waves. The data seem to in-dicate that waves in the frequency range between 0.12 and 0.7 Hz are subject to some damping by an oleyl alcohol surface

Fig. 1. Aerial photograph taken from an altitude of 450 m of a 2.3 km² oleyl alcohol experimental slick (Marsen experiment, September 1979).

film. This may be accounted for if it assumed that the surface film influences wave-wave interactions and/or the wind coupling [Barger et al., 1970], because a direct effect of such surface films on wave damping is confined to frequencies greater than 2 Hz, as has been shown by wave tank experiments [Hühnerfuss et al., 1980].

The question of the direction of energy transfer between short and long waves has been the subject of considerable debate in recent years. The observed wave damping (Figure 2) is compatible with the assumption that an energy transfer from short to long waves occurs. In the presence of the surface film, about 40–60% of the energy in the short wave spectrum is dissipated. This implies that less energy is available for transfer to the longer waves.

The wave attenuation value measured by the tower scatterometer is also included in Figure 2 and seems to be higher than that measured by the wavestaff at the same water wavelength. However, because of the overlapping error bars, it is

not yet clear if this is a real effect owing to a modification of the anisotropy of the wave spectrum in the presence of a slick [Hühnerfuss et al., 1980]. If such is the case, wave attenuation values would be different when measured by a wavestaff (no directional dependence) vis-a-vis a scatterometer with unidirectional dependence, and flight direction dependence of the observed wave attenuation values measured by airborne scatterometers would be expected. This has in fact been observed by Hühnerfuss et al. [1978], but large error bars associated with these measurements indicate the need for additional experimental verification.

Wave attenuation values owing to oleyl alcohol films have also been determined by evaluation of Doppler shift spectra measured by a tower-based radar [Hühnerfuss et al., 1980]. Again, a stronger wave damping is shown by these radar data in comparison with conventional wavestaff measurements, but owing to the large error bars, the authors would only tentatively conclude that the Doppler shift data show a directional
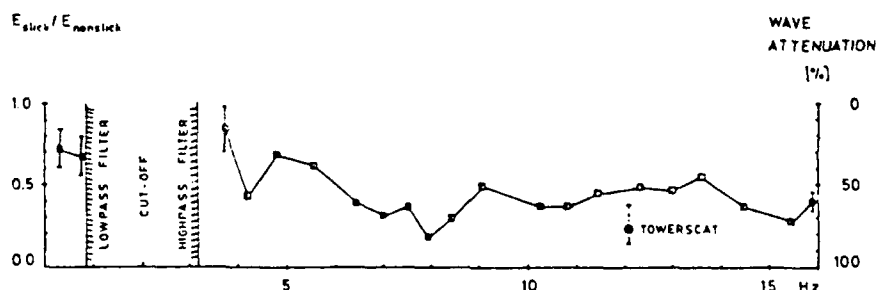
Fig. 2. The ratio of wave energy (slick/nonslick area) versus frequency measured by the vertical wavestiff. The scale on the right-hand side shows the corresponding values for the wave attenuation in per cent. Circled cross marks the value measured by the tower scatterometer [from Hühnerfuss et al., 1980].

dependency which is different in the presence of a sea slick.

During the Koff 74 experiment, oleyl alcohol surface films of smaller size were produced by method B, using a spiral flight pattern. The experiments were designed to study the chemical and the biological effects of artificial surface films and the modification of air-sea gas exchange caused by such films [*Brockmann et al.*, 1980]. Natural and experimental surface film samples were collected with a rotating drum skimmer [*Harvey*, 1966] several times during the 6-hour experiment. The samples were analyzed by gas chromatography for oleyl alcohol and for fatty acids, the latter serving as a tracer for the natural surface films. The data indicated that oleyl alcohol pushed aside the natural fatty acids in the sea surface during the spreading process. A slight increase of the fatty acid concentration in the samples taken from the experimental slick during the last 4 hours of the experiment was observed. This might have been due to natural surface active substances slowly entering the experimental slick from subsurface water, since relatively calm weather conditions prevailed and natural slicks existed around the periphery of the experimental surface film [*Hühnerfuss et al.*, 1977].

The surface 'cleaning effect' of the spreading oleyl alcohol suggested by the fatty acid data was confirmed by independent measurements of colony forming units (CFU) of heterotrophic bacteria [*Brockmann et al.*, 1980]. A strong reduction of CFU in surface samples occurred immediately after formation of the experimental slick. A slight additional decrease of CFU in the slick was observed after the slick had fully developed, which suggested that the oleyl alcohol surface film inhibited repopulation of the air-sea interface by the organisms.

Some of the slicks produced during the Koff 74 and Jonswap 75 experiments have been used to determine the drift responses of the slicks to wave and to wind action [*Lange and Hühnerfuss*, 1978]. The relative position of the slicks was determined by logging the direction and the distance from a fixed instrumentation pile to the slick's center with the helicopter. The helicopter's speedometer readings were corrected with the appropriate wind component. In connection with additional wind wavetank experiments, it could be shown that the tidal currents, wind, and gravity wave-induced Stokes drift obviously contribute to slick drift on the sea surface. A comparison of laboratory and field results indicated that the pure gravity wave drift component composes 25–30% of the total surface drift (without tidal current). Furthermore, monomolecular surface films proved to be a good tool for studying the surface drift because of their extreme thinness. Conventional surface floats generally indicate different drifts depending on their depth of immersion.

PRACTICAL APPLICATIONS OF SURFACE FILMS AT SEA

In recent years, several practical applications of organic surface films have been developed which are based upon small-scale modifications of the physical properties of the air-sea interface. One of the most notable manifestations of a slick, a consequence of its effects on capillary waves, is its high visibility under most conditions. The decreased average wave slope within a slick produces a light reflectance anomaly so that the affected area may appear either lighter or darker than the surrounding rippled water surface, depending upon the angle of view with respect to the sun. It was the high visibility of slicks produced by small quantities of certain organic substances that was the basis for the development of a novel sea

marker package for rescue and recovery operations at sea [*Garrett and Barger*, 1972].

This application of organic surface films is depicted in Figure 3, an aerial photograph of three seamarks taken from an altitude of 200 m. The upper surface mark is a wave-damped zone elongated in the direction of the wind. This chemical sea marker was generated by a floating package composed of oleyl alcohol and sodium fluorescein (uranine) dye mixed with chemicals that generate carbon dioxide gas bubbles upon contact with water and gradually dispense the slick. The center mark (barely visible) is a narrow band produced by a standard search-and rescue dye marker package composed primarily of sodium fluorescein, a water soluble fluorescent chemical. The lower slick patch in the figure was formed by the release of 27 g of oleyl alcohol from a subsurface, seltzer-type slow-release dispenser. At this viewing angle, the slicks appear dark, because the sun glitter pattern that reflects light toward the observer is weak where capillary waves are absent. The dye-only pattern (center) is barely visible under these viewing conditions. At certain other viewing angles, on the other hand, the slick detectability is poor, and the dye marker is more apparent. Consequently, both dye and surface film sea markers are used together to assure visibility at all angles and to increase the distance at which a mark on the sea surface can be detected. Furthermore, it has been demonstrated that oleyl alcohol surface slicks are detectable by X band radar, making them sensible from aircraft under many weather conditions and at night as well as by day.

Another application of artificial sea slicks that has been proposed is the enhancement of underwater visibility through the use of organic surface films. In folklore as well as in modern practice, fish oils have been used to calm the sea surface and to clarify the underwater scene. For example, divers sometimes carried and released such surface-active oils to mollify the sea surface and to reduce underwater shadows and bright spots caused by wave-induced refractions of light. To test the validity of this notion, 0.085 km^2 artificial slicks were generated in July 1970 above the Tektite II habitat, which rested in 17 m of water in Lameshur Bay, St. John Island, U.S. Virgin Islands. On the basis of previous research [*Barger and Garrett*, 1968], oleyl alcohol was selected for this application because it would produce a calmer, more intensely damped sea surface than either fish or vegetable oils. Photographic and visual observations were obtained by divers in the water beneath the surface film. Similar observations of underwater objects were made from vantage points above the sea surface before and after slick passage. Relative irradiance data and sun angles were measured for these experimental situations. A number of experiments were performed in the neighborhood of the Tektite II habitat in 17 m of water and in shallower water elsewhere in Lameshur Bay. In this series of underwater observations, there were no visual, photographic, or irradiance data that indicated significant visibility enhancement within the underwater environment because of the modification of the water surface by the artificial slicks and the attendant decreases in wave slope.

On the other hand, the visibility of underwater objects observed from above the air-water interface was greatly increased by the glassy water surface condition produced by the additive slick. The multiple relected images of the sky caused by the numerous small waves were eliminated, and the water surface approached that of a glass plate on which there were only minor perturbations caused by gravity waves. Details of

Fig. 3. Aerial photograph of three seamarks taken from an altitude of 200 m. Upper mark: Oleyl alcohol and sodium fluorescein (uranine) dye; center mark: standard search-and-rescue dye marker package (primarily sodium fluorescein); lower mark: experimental slick formed by the release of 27 g oleyl alcohol.

underwater objects that had been obscured by the multiple reflection pattern of a rippled surface could be seen clearly through the smoothed air-water interface when the slick was present. This effect was demonstrated by photographs and by observations of the undersea habitat whose uppermost portion was about 7 m below the surface of the water. When viewed through a rippled surface in the absence of a wave-damping organic film, only the blurred outline of the habitat could be discerned while objects with smaller dimensions could not be visually resolved. Viewing downward through a ripple-free film-covered surface, one could clearly see the major segments of the habitat and smaller features such as flanges and bolts could be identified, whereas they could not be seen without the surface film.

A third application of water-insoluble film-forming agents is directed at environmental protection. Organic chemical films that reduce the surface tension of water have been developed to confine and to control spills of petroleum products on water [Garrett and Barger, 1972; Garrett, 1969]. The application of suitable film-forming agents to the water around the edge of an oil spill reduces the water surface tension, one of the principal forces causing oil to spread into thin layers. The unmodified surface tension of the oil and the oil-water inter-

facial tension can then draw the oil layer into a significantly smaller area of greatly increased thickness. Decreasing the area of the oil film with surface-active chemicals does not cause emulsification or dispersal of the oil into the water but confines it on the water surface. Because oil-collection devices perform with greater efficiency on thicker oil layers, the use of chemical film to control oil on water has been adopted as a viable oil-spill control technique.

FUTURE RESEARCH

Organic Film Sea Truth for the Interpretation of Remotely Sensed Signals

It is evident from the wave attenuation values measured by wavestaffs during Jonswap 75 (Figure 2) that the decrease of L band (15-30 cm wavelength) radar cross section is expected to be almost as large as for K_u band (1.7-2.4 cm wavelength), since the wave damping was not strongly dependent on water wave frequency in the range from 3.2 to 16 Hz. Thus many ocean surface features which are discernible on L band SEA-SAT SAR images and which possibly indicate the presence of internal waves, oceanic fronts, current boundaries (e.g., Gulf Stream), and Langmuir cells, might be explained by a nonuni-

form distribution of monomolecular organic surface films. Consequently, simultaneous wave measurements by wavestaffs and L band radars of nonslick and slick-covered ocean areas would provide some of the 'sea truth' needed for the proper interpretation of remotely sensed signals.

Wave attenuation rates measured by K_u radars in the presence of an oleyl alcohol surface film seem to be higher than those measured by conventional wavestaffs [*Hühnerfuss et al.*, 1980]. It is presumed that wave damping caused by surface films shows a directional dependence which is resolved differently by wavestaffs (omnidirectional) than by the relative back-scattered power received by a K_u band radar (unidirectional) or by the directionally dependent resolution shown by the spectra of the Doppler shift. To confirm this hypothesis and to improve the evaluation of radar data in the presence of natural slicks, measurements of the wave attenuation rates with both wavestaffs and radars (with different directions of observation) should be performed on slicked and nonslicked sea surfaces.

Natural surface films consist of a wide variety of different surface active compounds which may interfere with the wind-wave field in various ways. Therefore, several compounds characteristic of natural slicks should be used for generating experimental surface films for the studies proposed in the preceding paragraphs.

Wind-Wave Coupling

The wave attenuation due to surface films can result from (1) direct influence of the film, (2) modification of short-wave-long-wave interactions, and (3) modification of the wind energy input. Whereas basic studies of the first and the third can be performed in wind-wave tanks by using different organic chemical films, wave-wave interactions must be investigated in situ with very large slicks, which for statistical reasons should permit a 30-min period of measurement. Open sea experiments should be conducted to provide additional information on the modification of wind-wave interactions by surface films for comparison with the experiments of *Barger et al.* [1970]. These studies should include air turbulence measurements directly above the waves with a wave follower and the use of surface films formed from chemical compounds with different interfacial properties.

Wave-Wave Interactions

The Jonswap 75 data [*Hühnerfuss et al.*, 1980] seem to indicate some damping of longer gravity waves in the frequency range 0.12–0.7 Hz by oleyl alcohol films. This influence should be confirmed by experiments with a slick of several square kilometers in area, one which would allow a long period of wave measurement for quantitative calculations of wave-wave interaction processes. Studies of experimental slicks formed from chemical compounds with varying influence on the capillary wave spectra are recommended as a means of gaining further insight into the coupling mechanisms between short and long waves.

Air-Sea Exchange of Organic Material

In recent years, several authors have stressed the importance of the transport of organic materials from the ocean to the atmosphere [*Barger and Garrett*, 1976; *Hoffman and Duce*, 1974]. Furthermore, organic surface films accumulate organic and inorganic materials as well as biological entities, so that fractionation occurs during air bubble bursting processes, and

the relative concentrations of the chemical and the biological species in the ejected drops are different from those in the sea. Quantitative calculations concerning fractionation processes could be improved by in situ studies of experimental surface films with specified physicochemical characteristics. Atmospheric samples would be taken directly above the slick area and upwind of the slick for subsequent chemical and biological analyses, and appropriate wind and wave measurements would be made.

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Experimental Sea Slicks in the MARSEN (Maritime Remote Sensing) Exercise

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EXPERIMENTAL SEA SLICKS IN THE MARSEN
(MARITIME REMOTE SENSING) EXERCISE

BACKGROUND

During the late summer and early fall of 1979, the Maritime Remote Sensing (MARSEN) experiment was conducted in the German Bight region of the North Sea. MARSEN was an international, multidisciplinary exercise involving numerous investigators and institutions from the United States and seven Western European countries. The Office of Naval Research coordinated the participation of the U.S. investigators. The project emphasized studies of the interactions of surface wind, waves, currents, and storm surge, using a wide variety of measurement methodologies including remote sensing. The ultimate goal of the experiment was to construct a storm surge/wind-wave prediction model which incorporates the interactions of various wind-wave fields and the variable bottom topography.

One aspect of the exercise involved the production of large monomolecular sea slicks to simulate natural organic surface films. Selected measurements were performed to determine the effects of the experimental slicks on air-sea interfacial processes and on remotely sensed surface phenomena. In coordinated experiments, these nontoxic surface films were generated upwind of the German research platform Nordsee, so that they drifted across the fields of view of microwave sensors and areas measured by wavestaffs mounted on the platform. In addition, the slick experiments were scheduled to coincide with flights of instrumented NASA aircraft.

The development of experimental slick technology has been reviewed in previous NRL reports [1,2]. These slicks are water-insoluble, organic films formed on the sea surface, which have been utilized for practical applications (seamarking, oil-spill control, etc.) as well as for fundamental studies of air-sea interactions [2]. In recent years experimental slicks have been used in a number of oceanic research projects to study their effects on wind-wave interactions [3,4], microwave backscatter [5], wave-wave interactions [6], and chemical and biological distributions at the air-water interface. The importance of experimental surface films for air-sea interaction research and remote sensing interpretation is discussed in the present report to illustrate their usefulness and future research potential. Selection criteria for slick-forming chemicals and film-generation techniques are included as part of the developmental research performed in preparation for the MARSEN exercise.

RATIONALE FOR RESEARCH WITH EXPERIMENTAL SLICKS

Surface-active organic material adsorbs at and spreads over the air-water interface. Natural slicks at sea associated with windrows, internal waves, calm water, and plankton

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blooms are thin films of biogenic polar organic matter at a sufficient surface concentration to modify physical interfacial properties. In general, sea surface films are monomolecular organic layers, which often exist at film pressures below those at which the film physically collapses and which may be thought of as two-dimensional gases or liquids. The film pressure vs area curve for a monolayer is analogous to the pressure vs volume curve for a gas. Surface tension is reduced by the organic film on water, and the degree of surface-tension reduction is the film pressure.

Small-scale hydrodynamic and physical processes at an air-water interface are modified by slicks at low film pressures, at a surface concentration where the film undergoes a transition from an expanded gas-like state to a state with liquid or solid properties. At this transition point the air-water interface is no longer "free," but is immobilized by the film. This effect has been clearly demonstrated by experiments on the capillary wave damping by water-insoluble organic surface films [7] and measurements of the influence of surface film pressure on water surface temperature and convective processes near the interface [8].

Adsorbed surface-active material not only attenuates existing waves but also inhibits wave formation [9,10]. According to Miles [11], the addition of a sufficient quantity of a soluble surface-active agent to produce an inextensible film at the air-sea interface can increase the minimum wind velocity necessary to produce waves by almost one order of magnitude. While natural sea slicks should in theory withstand winds of this order (12 m/sec), their constituents are dispersed at sustained wind speeds of from 5 to 7 m/sec and sometimes less. The concentration of surface-active material in the underlying seawater is usually insufficient to supply and maintain a coherent surface film under highly dispersive conditions.

On the other hand, artificially produced surface films of water-insoluble organic compounds may possess the wave-inhibiting properties against winds as high as 12 m/sec. On several occasions artificial slicks have been formed and maintained for a period of time when winds were as great as 10 m/sec. Even under these adverse conditions, coherent experimental surface films could be maintained as long as excess film forming material was present to repair ruptures in the man-made slick caused by dynamic processes at the air-water boundary.

The various effects of both natural and experimental surface films on air-sea interfacial properties and processes are reviewed in Table 1. In addition to the previously mentioned capillary-wave and surface-temperature effects, natural films modify bubble bursting characteristics and sea foam, alter electromagnetic wave reflection by attenuating capillary and small gravity waves, and act as an interfacial organic phase which accumulates oleophilic pollutants. Wave attenuation and ocean surface temperature effects have been studied using large experimental slicks at sea, while other film-induced modifications of interfacial properties have been demonstrated solely in the laboratory.

Most of the numerous effects of natural slicks (Table 1) may be duplicated by experimental surface films composed of selected pure compounds. These interfacial modifications may be caused by a wide variety of water-insoluble surface films which modify the microscale hydrodynamics and the rheology of the air-sea interface. It will be shown in ensuing sections that certain substances can be used to produce experimental sea slicks which are useful for fundamental studies of wave-wave and wind-wave interactions and for the evaluations of the effects of sea surface films on the interpretation of remotely sensed signals.

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Table 1 — Impact of Natural and Man-Made Surface Films on Properties of
the Air-Sea Interface

Surface Effect or Process Modification Studied	General Results and Literature References	
	Natural Surface Films	Experimental* Surface Films
Capillary Wave Attenuation	++ [12] [13] [17] \ [14]	++ [4] ++ [6]
Gravity Waves	- [12]	++ [4] ++ [6]
Breaking Wave Inhibition	? -	++ [4]
Gas Transport Reduction	? -	+ [8] ++ [15] + [16]
Oleophilic Pollutant Accumulation	++ [17] [18] [19]	? -
Foam Stability	+ [20]	+ [21]
Air Bubble Bursting	+ [22] [23]	+ [23] [24]
Surface Temperature	++ [25]	++ [26] + [8] + [27]
Electromagnetic Wave Reflection	++ [28] [29] [30]	++ [4] [5]

- significant influence of surface film unlikely; ? potential influence, but not proved by experiment;
+ demonstrated in laboratory, field studies if any were inconclusive; ++ effect demonstrated by labora-
tory and field research; * a continuous, monomolecular film added to water surface for research
purposes.

The influences of natural organic sea surface films on remotely sensed signals are
reviewed in Table 2. Since natural slicks attenuate and resist the formation of capillary
waves, affected sea surface areas have different electromagnetic or light reflectance charac-
teristics than those of surrounding nonslicked waters. When passive reflectance is sensed, the
relative intensity of the signal is dependent upon the observation angle, the relative position
of the sensor with respect to the sun, meteorological conditions, and other factors. With
active sensors such as microwave radar, the power of the backscattered radiation is sharply
reduced by the ripple-damped sea surface under the influence of the organic film.

In general, natural slicks appear slightly cooler than adjacent water surfaces when
sensed by thermal infrared [25]. Although the emissivity of a planar water surface is not

Table 2 — Effects of Natural Organic Seasurface Films on Signals Received by Remote Sensing Systems

Seasurface Effect	Sensor Approach—Spectral Region	Influence on Signal
Capillary wave damping	Active reflectance—microwave radar Passive reflectance—UV, visible, near IR	Reduced backscatter power Modified light reflectance
Inhibition of convective overturn at surface	Passive emission—thermal IR	Slicks appear cooler
Inhibition of wave breaking Modified sea foam stability	Passive emission—microwave	Affects brightness temperature
Reduced seasurface roughness	Passive—microwave	Reduced brightness temperature

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altered by the presence of a monomolecular layer of organic material [31], the cool-surface effect is produced by an immobilization of the near surface water by the relatively rigid surface film, thereby inhibiting convectional overturn of the water cooled by evaporation in the surface microlayer [8]. Warm signatures of natural sea slicks have not been observed by thermal infrared sensors, since they are not expected to retard evaporation to a significant extent. When passive microwave radiometers are used to sense the sea surface, the observed signal depends upon emission and reflection from the structured air-water interface. Experimental oleyl alcohol slicks were sensed by airborne radiometers operated at 1.4 (K_u band), 8.35 (X band), and 14.5 (L band) GHz [32]. The monomolecular film on the sea surface affected the radiometric signals in the same way as would a decrease in surface roughness. The oleyl alcohol slick was manifested as a $2°K$ decrease in antenna temperature with X and K_u bands for both horizontal and vertical polarizations. No detectable effects were observed with L band. Since the slick damped the capillary wave spectra and was readily detected at the shorter wavelengths, it was concluded that small-scale roughness is an important parameter affecting emission from the sea surface.

Passive microwave sensors can also detect sea foam through a resulting increase of sea surface emissivity. Air bubbles and foam at the air-water interface are responsible for the passive microwave signals, while entrained air bubbles beneath the surface do not contribute to the effect. Surface-active material modifies sea foam through several mechanisms. Insoluble surface organic films may decrease wave breaking and also act to destabilize foams and bubbles once they reach the water surface. Water-soluble, surface-active materials, on the other hand, are foam stabilizers. The net effect of these opposing processes has not been determined experimentally at sea.

When petroleum spills or municipal effluents are present, thicker films are implicated in the production and modification of remotely sensible signals. The influences of petroleum films on remote sensing are similar to those of natural slicks, except for thermal IR sensors, to which a petroleum surface film may appear either cooler or warmer than adjacent clean water. The sensed IR signal may be due to a number of possible physical effects, the relative importance of which has not been demonstrated by sea-truth experiments.

Petroleum spills may be sensed across a broad spectral range by numerous sensor systems. Because oil spills vary greatly in thickness and in their physical and chemical characteristics, the portion of the spill sensed varies according to the sensing system used for observation. For example, microwave radar senses the entire area affected by the oil in which the capillary wave structure is attenuated, whereas dual-frequency, passive microwave radiometry senses only the thicker layers of the spill and can be used to determine spill thickness and volume. Both natural surface films and pollutants may be incorrectly identified as petroleum by many remote sensing devices. Under certain circumstances the use of multispectral sensing systems is required to avoid ambiguities.

In most instances sea truth must be determined if remotely sensed data are to be correctly interpreted. For example, reduced sea surface return of microwave radar signals may be due to the following sea-truth situations in which capillary waves are either diminished or absent; (1) zones of calm where no organic film is necessarily involved, (2) hydrodynamic damping in a ship's wake, (3) wind slicks, (4) natural sea slicks caused by organic films which attenuate and resist the formation of capillary waves, and (5) thicker layers of

wave-damping petroleum oils or other organic film forming pollutants. Other sensors used for the detection of oil on water also have a number of possible false alarms which require measurement and observation at the air-sea boundary to ascertain corresponding sea truth. The experimental slicks discussed in this report may be used to "calibrate" remote sensing systems to assist in the interpretation of sea surface events.

EXPERIMENTAL APPROACH

Criteria for the Selection of Slick-Forming Materials

Several physical and chemical criteria must be considered in the selection of a mono-layer-forming material for the creation of a durable, continuous, and capillary-active experimental sea slick. The molecule of the slick-forming material should contain both polar and nonpolar functional groups; a hydrophilic group which adsorbs at the water surface and a hydrophobic hydrocarbon chain which is oriented away from the water surface when the film is under lateral pressure. The material must spread spontaneously over the water surface as a water-insoluble monomolecular film so that only small quantities are required to affect a large water surface area. The hydrocarbon portion of the molecule should contain at least 18 carbon atoms so that losses from the slick due to evaporation and dissolution will be small. A nonionic, film-forming chemical is required for use on saline water to obviate reaction with ionic species which would increase film solubility. Commercially available materials which satisfy these requirements include fatty alcohols and esters, glyceride esters of fatty acids (vegetable and fish oils), and several synthetic surface-active agents. Table 3 is a list of

Table 3 — Properties of Film-Forming Materials for the Production of Persistent, Highly Surface Active, Experimental Sea Slicks

Highly Surface Active—Strong capillary wave damping
                  Resist generation of air-water interfacial
                      disturbances

Liquid—Easily and rapidly spread onto water surface

Nonvolatile—Low evaporative loss rate

Nonionic—Little reaction with saline water to ensure film persistence

Low Water Solubility—Long film persistence

Fluid Monomolecular Film—Rapid, spontaneous spreading
                    High respreading potential

Low Freezing Point—Effective fluid films in cold environments

Nontoxic—Ecologically acceptable

properties required for substances to be used for the production of persistent, highly surface-active, experimental slicks on the sea. Initial experiments were performed in the laboratory and on the Chesapeake Bay to determine (a) the feasibility of creating and sustaining a monomolecular film on the sea; (b) the resistance of various experimental surface films to natural dispersive forces of wind, waves, bursting bubbles, *etc.*; (c) the most effective monolayer-forming materials for the creation of a durable experimental slick for various applications and research purposes; and (d) the quantity of surface-active material required.

For comparison purposes a series of experimental slicks of different substances was produced simultaneously from point source applications. The slicks were made from the following film-forming materials:

oleyl alcohol (9-octadecen-1-ol, cis isomer) an 18-carbon, monounsaturated fatty alcohol, equilibrium spreading pressure = 31 mN/m.

cottonseed oil, glyceride esters, whose fatty acids are primarily palmitic C_{16}, oleic $C_{18:1}$, and linoleic $C_{18:2}$, equilibrium spreading pressure = 14 mN/m.

oleyl ether containing two oxyethylene groups, equilibrium spreading pressure = 42 mN/m.

isostearyl alcohol containing two oxyethylene groups, equilibrium spreading pressure = 44 mN/m.

oleic acid (9-octadecenoic acid, cis isomer), equilibrium spreading pressure = 30 mN/m.

sorbitan monooleate, equilibrium spreading pressure = 42 mN/m.

Since the slicks were deployed at approximately the same time, they were subjected to similar environmental stresses. These studies were performed several times with small quantities (25 to 150 ml) of film-forming substances so that the slicks could be observed and their dimensions measured during their lifetimes. The relative slick lifetimes and their capillary wave damping intensities were nearly identical for each series of simultaneously produced slicks. These studies were performed under conditions of steady winds (4 to 7 m/sec) with no natural or pollutant slicks in evidence.

During the first 20 to 30 min all of the slicks grew equally to a size determined primarily by wind-driven surface water flow. During this period excess film-forming material in equilibrium with the spread film was sufficient to overcome losses from the slick due to natural processes. After a period of about 30 min the more water soluble films, *e.g.* oleic acid, no longer increased in surface area. The less soluble films continued to increase in areas at about equal rates. At a slick lifetime of about 1 h, three of the moderately soluble slicks, sorbitan monooleate, isostearyl alcohol (2-oxyethylene groups), and oleyl ether (2 oxyethylene groups) disappeared rather suddenly over a short time period of from 5 to 10 min. Their constituents were no longer at a sufficiently high surface concentration to alter capillary waves and other small-scale interfacial dynamic processes. Since these effects modify light reflectance from a slick-covered water surface, the slicks in question were no longer visible. Oleyl alcohol and cottenseed oil are quite water insoluble even in monomolecular layers,

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and their films persisted about three times as long as any of the others studied. Film life-time is an important aspect when using experimental slicks for basic and applied purposes because of the difficulty in maintaining a one-molecule-thick organic layer against n. ural dispersive processes. Consequently, oleyl alcohol and cottonseed oil are examples of mate-rials with relatively high and moderate film pressures which can be used effectively to pro-duce persistent experimental slicks on bodies of water.

During the simultaneous observations of the adjacent slicks it was noticed that the capillary wave damping in the low-film-pressure slick of cottonseed oil was less intense than for the other experimental films whose film pressures were 30 mN/m or greater. More high-frequency wave structure was visible in the cottonseed oil slick, and its light reflectance effects were less pronounced, having the appearance of natural slicks with similarly low film pressures [7]. In the laboratory most surface films damp mechanically generated capillary waves to approximately the same degree when their film pressures are on the order of a few millinewtons per meter [7]. However, in the open-water studies the surface films were at their maximum spreading pressures in equilibrium with unspread droplets of film-forming material. The film pressure of the slicks with strong capillary wave effects (greater than 30 mN/m) was more than twice that of the less effective cottonseed oil film (14 mN/m). Thus the resistance of a slick to capillary wave formation is not solely related to its wave-damping characteristics as measured in the laboratory with mechanically generated ripples. It is not yet known which physical parameters of an organic surface film govern its influence on capillary waves at sea. It has been observed, however, that slicks with high film pressures damp water waves and small-scale turbulence more intensely than those of lower equilibrium film pressures.

Because of its long lifetime and strong surface effects, oleyl alcohol has been used for most experimental sea slick studies. In addition, this material meets the criteria listed in Table 2. On the basis of these criteria, cottonseed oil and methyl oleate are also suitable for the production of persistent slicks, except that with their lower film pressures they more closely simulate natural films in their physical effects on interfacial properties and processes.

Techniques for Generation of Experimental Slicks

A—Dispensing Film-Forming Material from a Surface Vessel

When organic surface-active material is placed on a clean water surface in the absence of wind, it spreads spontaneously in all directions. Its initial spreading velocity varies between 34 and 40 cm/sec for the types of film-forming materials discussed in this report. The spread-ing velocity is related in part to the equilibrium spreading pressure of the surface active material [33]. The spreading velocity decreases rapidly with distance from the source of the film-forming material, decreasing to 10 cm/sec or less when the leading edge of the film is 3 m from the point of application. Under the influence of wind, however, the film is moved along with the flow of the surface water (3 to 4% of the wind velocity), and the excess bulk material which exists as floating lenses also moves with the wind-driven surface water flow. The rate of motion of the downwind edge of the slicks is the sum of the surface water flow

and the film spreading velocity at that point. Thus, a point source addition of spreading oils under the influence of wind produces an elongated slick whose dimensions are primarily a function of wind velocity and surface current.

It is also possible to generate a slick by continuous dispensing from a vessel moving in a direction perpendicular to the wind. However, a stripe of slick does not grow uniformly, but eventually forms streaks along the downwind edge. Thus, in order to produce a large slick for experimental purposes which has a circular or rectangular shape, it is necessary to "paint" the slick-forming material onto the water surface. That is, it cannot be simply dispensed from a point source or a single stripe, but must be laid in adjacent bands or in an expanding spiral from either a surface vessel [3,4] or an aircraft [2,5].

B—Generation of Slicks by Aerial Dispensing of Frozen Oil Cubes

Several problems are associated with the production of experimental slicks from a surface vessel. The vessel may disturb the natural wave and turbulence fields and possibly emit interfering chemical pollution. In addition, there is a requirement for the production of large slicks several square kilometers in area in a relatively short time. Thus, an alternative method for the generation of experimental sea slicks has been developed, whereby frozen chunks (oil cubes) of the film-forming material are systematically distributed from a helicopter. During projects in 1974 [34] and 1975 [5], 80-g chunks of 96.5% oleyl alcohol (9-octadecen-1-ol, cis isomer) were prepared by freezing the material to 249°K in small paper cups. The frozen chunks were transported in large Dewar containers for dispensing from the helicopter.

If surface currents prevail during slick-forming operations, it is essential to drop several chunks to produce a sample slick prior to formation of the main experimental surface film. Thus, one can observe the spreading characteristics and direction of drift of the sample slick with respect to a fixed point, such as an anchored ship or instrumentation pile. This procedure is necessary to assure that the main experimental slick will drift through an array of wave-measuring and meteorological instruments or through the fields of view of sensors being used in conjunction with the slick research.

As mentioned previously, natural forces displace the slick-forming material from the air-sea interface. The rate at which this occurs is a function of the intensity of the dynamic processes operating on the interfacial film. To maintain a continuously slicked sea surface area, it is necessary to dispense an excess of film-forming material over that required to form a monomolecular film. The excess material does not increase the slick thickness above that of a monolayer, because the film-forming materials selected are autophobic, *i.e.*, they do not spread over their own monomolecular film. Thus, the excess material exists as unspread floating drops in equilibrium with the fully compressed slick. When a portion of the slick is dispersed by natural processes, the excess film-forming material represents a floating reservoir to rapidly replace the lost organic material and restore the equilibrium pressure of the surface film. The surface concentrations (liters-km^{-2}) used successfully in various experimental sea slick studies are listed in Table 4. The quantities used can be compared with that required for a single molecular layer of oleyl alcohol, 1.75 l-km^{-2}.

Table 4 — Quantities of Oleyl Alcohol Used in the Production
of Various Experimental Sea Slicks

Dispensing Mode	Slick Size (km^2)**	Oleyl Alcohol Volume (liter)	liters-km^{-2}	Reference
Boat*	0.50	13.0	26.0	[4]
Boat*	0.70	19.0	27.1	[3]
Fixed-wing Aircraft*	0.52	18.0	34.6	[2]
Point Source	0.005	0.1	20	[35]
Helicopter+	1.5	30.0	20	[5]
Monolayer, theoretical	—	—	1.75	—

*Dispensed as a liquid stream from a pressured container
**Maximum area of slick during its lifetime
+Frozen, 80-g chunks dispensed periodically

EXPERIMENTAL SLICKS IN THE MARSEN EXERCISE

Three monomolecular, organic surface films were produced as part of the MARSEN exercise in the vicinity of the German research platform Nordsee (Fig. 1) located at 54° 42' 33" N, 7° 10' 7.4" E, in the North Sea. This location is about 72 km west of the southern end of Sylt Island and 72 km northwest of Helgoland Island. The upper deck of the research platform is about 28 m above mean water level and the water depth is 30 m. The experimental slicks were generated approximately 1.5 km upwind of the platform, so that they would drift across the footprints of various sensors mounted on the platform. In addition, the slicks were coordinated with overflights by instrumented NASA P-3 and CV-990 aircraft.

The experimental slicks were produced by dispensing frozen blocks of film-forming material from a helicopter flying at an altitude of 30 m above the sea surface. The blocks were dispensed at calculated intervals as the helicopter flew a series of parallel tracks perpendicular to the calculated surface drift in order to develop a continuous, approximately square surface film.

The initial center point of the dispensing pattern was calculated from tide tables and the ambient wind velocity and direction data obtained by radio from the platform. A test slick formed from several blocks of film-forming material was allowed to develop and move for several minutes to provide a final test of the direction of slick drift. These precautions were a necessary part of the slick-laying procedure to ensure that the experimental film would pass with its center near the platform and influence the wavestaffs and microwave sensors to the greatest extent possible.

The characteristics of the three slicks generated for the MARSEN exercise are reviewed in Table 5. Both slick-forming compounds were obtained from the Henkel Co. poration, Dusseldorf, West Germany. The oleyl alcohol has a purity of 96.5%, and a freezing point of 4 to 6°C. The methyl oleate was a technical grade material (74.8%) with a freezing point at -6° C. Although the latter substance was not of high purity, its surface-chemical properties and capillary-wave damping characteristics were closely similar with those of high-purity methyl oleate (99%+) according to H. Hühnerfuss of the University of Hamburg, Hamburg,

Fig. 1 — Research platform, Nordsee, located in the German Bight section of the North Sea (54° 42' 33"N, 7° 10' 7.4"E) and used as focal point of MARSEN coordinated slick experiments. Helicopter pad is located at the southeast quadrant of the platform.

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West Germany. During the slick experiments the wind was generally from the west at 10 to 16 knots, there were few whitecaps, and no natural slicks were evident. Film pressures measured by the calibrated spreading oil technique were essentially zero, indicating that no natural coherent surface films existed in the dynamic sea surface.

Slick number 2 depicted in Fig. 2 was formed from methyl oleate (9-octadecenoic acid, methyl ester, *cis*), a substance whose film pressure is about one-half that of the oleyl alcohol used in the other two experiments. The degree of wave damping in the methyl oleate film was somewhat less than that caused by the oleyl alcohol films. This wave damping difference was readily discerned from visual observations and was measured by differences in the power of backscattered radiation from X- and L-band radars mounted on the research platform. The backscattered X-band signal was reduced about fourfold over that from the nonslicked sea surface, while the backscattered L-band signal was about twofold reduced by the methyl oleate film. The reductions of the backscattered power of the microwave radar signals from the methyl oleate film was on the order of 5 to 7 times less than those from the oleyl alcohol slicks which attenuated capillary waves and short gravity waves more intensely. Furthermore, the methyl oleate spread more slowly than oleyl alcohol and took longer to form a continuous film over the water surface. The slower spreading of the methyl oleate was due to two factors. First, since the spreading velocity of a monomolecular film increases with film pressure [33], the methyl oleate would be expected to spread more slowly from its source, the bulk material floating on the sea surface. Furthermore, because of the lower freezing point of methyl oleate, it was necessary to solidify it with dry ice. Consequently, considerable time was required for the frozen blocks to melt in the cool sea (14°C) to form liquid lenses from which the surface film could readily spread. Spontaneous spreading of a monolayer is considerably slower from the solid phase than from the liquid phase.

Experimental slicks 1 and 3 (Table 5) were formed from oleyl alcohol (9-octadecen-1-ol, cis isomer). Slick number 1 was produced in close coordination with overflights by NASA P-3 aircraft equipped with an Airborne Oceanographic Lidar (AOL) as well as other remote sensing instrumentation. The AOL was operated in three modes to sense the monomolecular slick as well as some of the chemical parameters associated with and modified by organic surface films on water; specifically fluorescent organic substances and chlorophyll. The experimental slick was sensed by its attenuation of laser-induced, water-Raman backscattered radiation. As the aircraft crossed the slick, the Raman signal decreased rapidly to a constant value near the edge of the surface film and increased again to a value indicative of clean nonslicked water when the aircraft was no longer above the film-affected area. Thus, this measurement clearly defined the film-covered sea surface area, and the dimensions of the slick could be calculated from the transit time and speed of the aircraft. The fluorescence and chlorophyll measurements as well as results from S- and L-band passive radiometric sensing of slick number 1 from the P-3 will be presented elsewhere.

Experimental slick number 3, the largest formed, was 2.3 km^2 in surface coverage and measured 1520 by 1500 m (Figs. 3 and 4). This nearly square surface film passed directly across the center of the platform. The slick drift velocity of 0.71 m sec^{-1} was determined by measurement from the helicopter and from the entry and exit time for the slick at the western edge of the platform. This value agreed well with a drift velocity (0.69 m sec^{-1}) calculated as a resultant of wind and current vectors. The calculated slick drift velocity was determined in advance of the experiment by assuming that the drift component due to wind

Table 5 — Characteristcs of MARSEN Experimental Slicks

Slick	Compound	Date	Dispensing Times*	Quantity (kg)	Size (km²)	Film Pressure (mN/n)**	Drift Velocity (m/sec)
1	oleyl alcohol	22:9:79	0814-0837	32.0	1.5	31	0.59
2	methyl oleate	28:9:79	1050-1120	32.8	1.0	15	—
3	oleyl alcohol	28:9:79	1200-1235	48.0	2.3	31	0.71

*Universal time
**Laboratory measurement at 25°C

Fig. 2 — Aerial view of a 1.0 km² monomolecular film of methyl oleate passing the Nordsee platform. The photograph looks toward the wind direction at 290°.
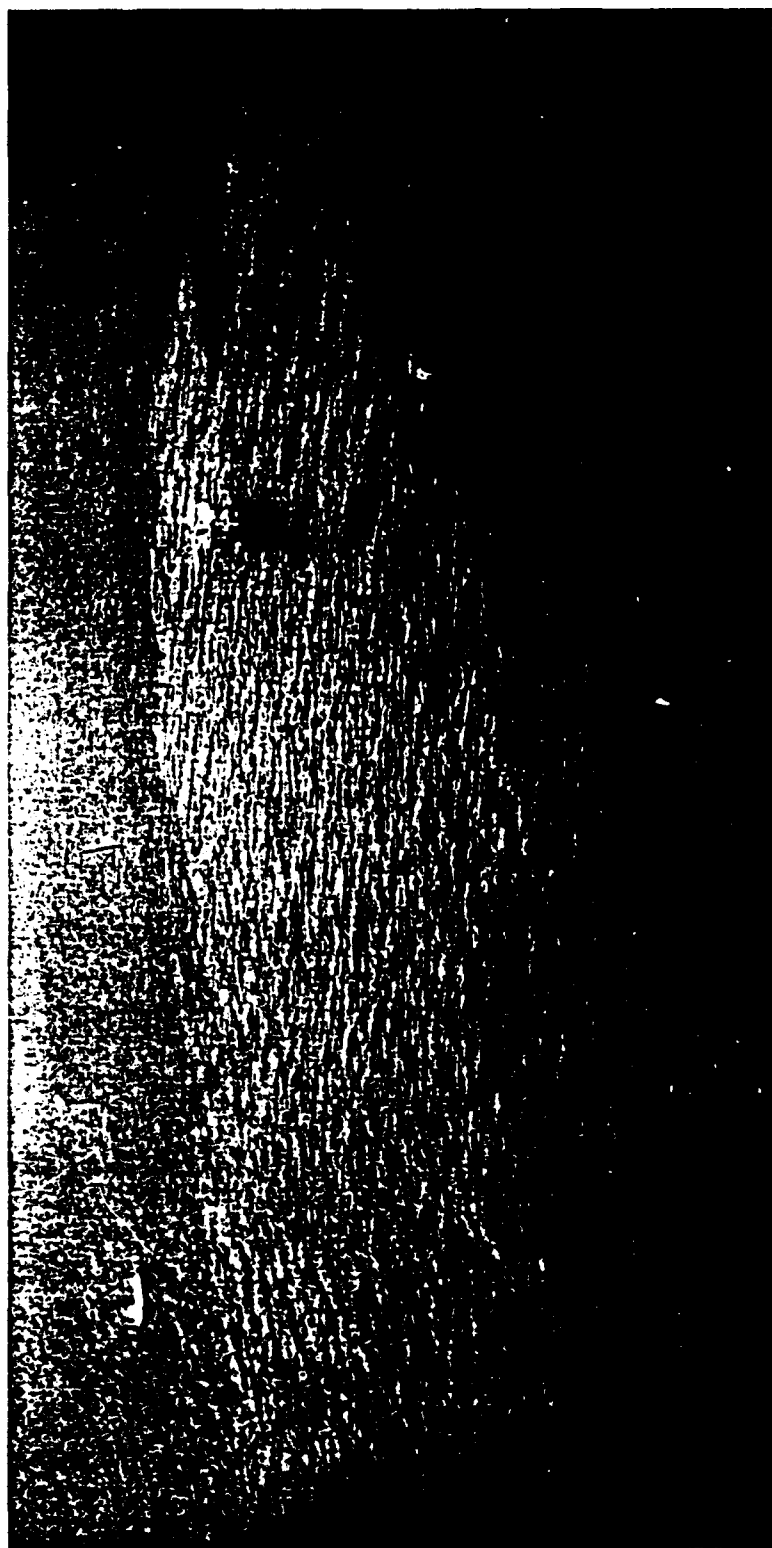
Fig. 3 — Aerial photograph of slick 3, a monomolecular film of oleyl alcohol, 2.3 km² in area passing the Nordsee platform, 28 September 1979 at 1230 UT
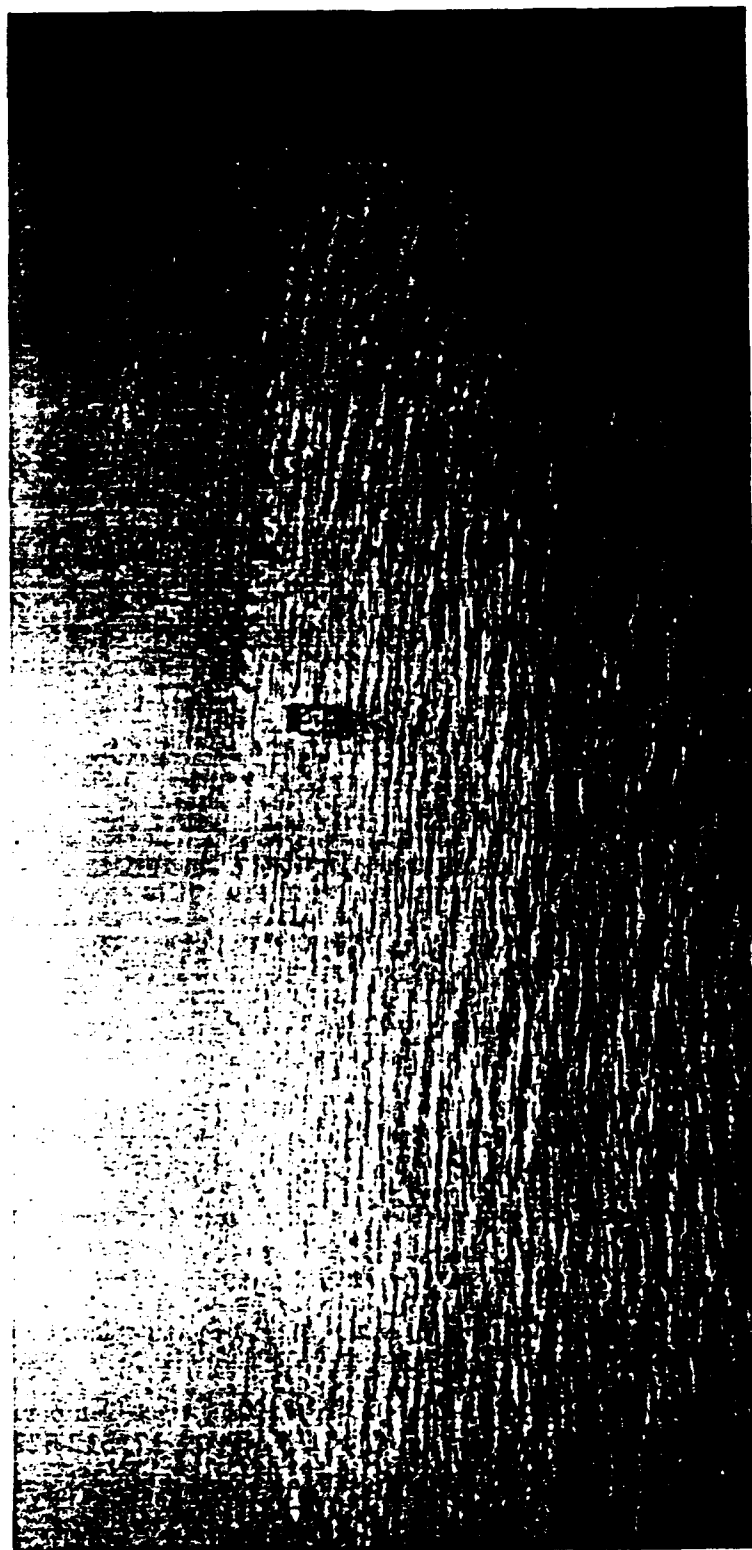
Fig. 4 — Aerial photograph of slick 3 looking west, 28 September 1979 at 1255 UT

was 3.5% of the wind speed. The transit time of slick 3 across any particular point of observation was about 35 min. This continuous slick was sensed by both X- and L-band radars and by wavestaffs capable of measuring the gravity wave spectra. Consequently, it is anticipated that the possible influence of the film on gravity waves and the role of capillary waves on the modulation of larger waves will be ascertained when the collected data have been analyzed by the MARSEN investigators involved in these measurements.

ACKNOWLEDGMENTS

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APPENDIX B

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INVOLVEMENT OF ORGANIC SEA SURFACE FILMS IN THE HIGHLIGHTING OF SURFACE AND UNDERWATER OCEANIC PROCESSES IN REMOTELY SENSED IMAGERY

The Problem of Sea Surface Film Persistence

Technical Report

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1.0 BACKGROUND

Organic sea surface films can modify the following hydrodynamic and air-sea interfacial processes.

- capillary and short gravity waves
- wave-wave interactions
- wind-wave interactions
- surface microlayer stability/temperature
- wave breaking
- bubble and foam stability
- gas and particle exchange

As a result of these surface film effects, a number of ocean phenomena can be highlighted in remotely sensed imagery. These include:

- internal waves
- Langmuir circulation, windrows
- frontal boundaries
- convergent zones over bathymetric features
- ship wakes
- eddies
- upwelling
- biological activity

Many of these oceanic processes originate beneath the surface and cause surface convergences or currents. These subsurface processes are manifested in remote imagery when organic films are formed or organized by the sea surface straining. For example, ship wakes, eddies, fronts, internal waves, current shears, and organic slicks (both natural and anthropogenic) have been imaged by space-borne Synthetic Aperture Radar (SAR) and photography. Any or all of these oceanic processes may be evident in the imagery depending upon environmental conditions, the type of sensor, and the sensor look angle and travel direction relative to the target. Sea Satellite (SEASAT) SAR imagery of sea surface features have been reviewed by Fu and Holt (1982), Vesecky and Stewart (1982), and by Kasischke et al. (1984).

Petroleum oil slicks and pollutant oils spilled into the turbulent wakes of ships have also been imaged by the SEASAT SAR and described in the foregoing literature. Natural organic sea slicks have been identified in space-based photography (Soules, 1970; Maul et al., 1974; and Maul, 1978). Kaltenbach et al. (1984) presents SIR-A (Shuttle Imaging L-band SAR) and sun-glint photography of spiral eddies. The surface flow patterns of these eddies are probably

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highlighted by natural organic films, which modulate the reflective characteristics of the sea surface through their ability to attenuate and resist the formation of capillary waves. Numerous examples of spiral eddies in fields of natural surface films also appear in sun-glint photography taken from the Shuttle Mission 41-G of October, 1984 (Scully-Power, 1986). In addition, the turbulent wakes of ships are clearly highlighted for distances as great as 50–80 kilometers by the extensive filigree pattern of sea-surface films. These sun-glint photographs represent an example of the involvement of organic films in the remote detection of sea-surface features.

The sun-glint pattern is observed when the angle of view equals the angle of incidence of the sun's rays on the sea surface. When the sea is roughened by waves, especially those in the capillary wave spectrum, a broad sun glitter pattern is produced with a diminishing brightness outward from the sub-solar point on the sea surface (Soules, 1970). According to Cox and Munk (1954), the farther a wave face is from the specular point, the larger its slope must be to reflect the sun's rays toward the observer. Thus, the brightness distribution in the glitter pattern is related to the distribution of wave slopes.

Within the sun-glitter pattern the slick-like features are brighter than the ambient sea surface, suggesting that the surface is more specular due to a smaller average wave slope caused by capillary wave suppression by organic sea surface films. Outside the glitter pattern the opposite reflectance contrast is observed; the slicks appearing darker than the surrounding water surface. In this latter instance, less skylight is reflected toward the observer from the less roughened sea surface zones.

2.0   NATURAL FILMS AND SHIP WAKES

Within and adjacent to the sun-glitter pattern, the turbulent ship wakes are highlighted by the filamentous and cloud-like slicks for distances as great as 80 kilometers. Within the sun-glint for a distance of several ship lengths behind the ship, the turbulent wake is as specular as the surrounding slick due to intensive turbulent damping of surface scatterers. Further behind the ship, the turbulent wake has roughened somewhat and appears as a darker narrow track through the slick field. When no pollutant oils are present in the turbulent wakes, as is usually the case, a slick-like band sometimes forms on either side of the wake. When no slicks are present (a clean sea surface), the turbulent wake is either not visible or is detectable for a few ship lengths.

The observations in the foregoing paragraph are consistent with the presumption that the turbulent wakes are rendered visible in space-based photography by their influences on the field of organic sea surface films. In this regard, a review of the physicochemical effects of organic films at the sea surface and their role in the interpretation of remotely sensed imagery has been

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published (Garrett, 1986). Figure 1 is presented in support of the argument that organic surface films are instrumental in the highlighting of turbulent ship wakes in sun-glint, space-based imagery. This photograph is of a ship of of opportunity in coastal waters west of San Diego, CA, and was taken from an altitude of 1,000 feet. When a ship passes through a field of slicks, its turbulent wake disperses the organic film-forming material from the sea surface, leaving a more choppy, slick-free path. A double surface convergence on either side of the turbulent wake increases the level of organic surface-active material in the sea surface to the point that two slick lines are formed at the outer edges of the wake. Wake surface convergences of this kind, as a consequence of wake hydrodynamics in a stably stratified ocean, were described and demonstrated with airborne thermal infrared imagery of ship wakes by Garrett and Smith (1984).

The ship wake photograph (Figure 1) shows a strong similarity to the turbulent wake signatures in the Shuttle sun-glint photography. There is a film-free path produced by the turbulent wake through a field of natural slicks, a convergence-generated double slick band on either side of the wake, and an extension of the two convergence slicks into nonslicked water. The extension of .'e convergence-generated slicks is due to the increase of the concentration of slick-forming material to a critical level where surface scatterers are damped and suppressed, and visible films are formed. This evidence strongly argues for organic film involvement in the highlighting of turbulent surface ship wakes in sun-glint photography from space. It is difficult to imagine that current modulation of capillary scatterers or that fields of different atmospheric stability would be responsible for ship-wake highlighting in the sun-glint imagery.

An experiment was conducted in 1986 (Kaiser et al.), which generated definitive evidence that organic surface films were involved in the railroad track signatures of turbulent ship wakes in remotely sensed optical imagery. Large freight ships produced the characteristic double convergence slick bands in an otherwise slick-free area of the Chesapeake Bay. The surface tension was measured across these turbulent wakes numerous times using the calibrated spreading oil technique (Adam, 1937; Zisman, 1941). Surface tensions within the slicked bands were 3-5 mN/m less than the tension value for the ambient clean surface. Between the convergence-generated slick bands behind the ship, the surface tension was substantially the same as the ambient surface. Thus, organic films are involved in highlighting ship wakes in sunglint images from space and may also be implicated in outlining other events such as eddies, fronts, and upwelling.

3.0   SEA SURFACE FILM PERSISTENCE

Organic films are implicated in the highlighting of the turbulent wakes of ship in sun-glint and synthetic aperture radar imagery. However, the long persistence of these organized films,

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Figure 1. Ship of Opportunity Passing Through a Field of Natural, Organic, Sea-Surface Films Between the California Coast and San Clemente Island

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estimated to be as much as five hours old, requires explanation. Recent research and modeling suggest that wake dynamics or entrained bubbles cannot account for these long-lived sea surface effects. Although the persistent films are observed at relatively low wind speeds, there is an intrinsic property of these monomolecular films to spread into a clean water surface and distribute their molecules evenly, in order to maximize surface entropy. Consequently, characteristics of weathered, natural organic surface film, which resist this spreading, may be part of the elusive explanation of the observed film persistence at sea.

Some experimental evidence and studies indicate that environmental processes modify natural films and influence their spreading over the sea surface. These studies include: (1) the effect of organic films on air bubble lifetimes at the sea surface, (2) hysteresis and compression-induced changes in film pressure versus area curves, and (3) photocatylatic oxidation and ultraviolet polymerization of natural films.

3.1   Sea Surface Bubble Stability

This section summarizes a publication by Garrett (1967), entitled "Stabilization of Air Bubbles at the Air-Sea Interface by Surface-Active Material." Bubble lifetimes were measured on freshly collected seawater using a 1 cm deep hydrophil tray and 2.0 mm bubbles released from near the tray bottom. The trough was filled with seawater, the water surface was swept clean with sliding hydrophobic barriers, and bubble lifetimes were measured at intervals during the film-aging period. The surface-active material, which had reached the water surface during the waiting period was then compressed in stages, and bubble lifetime (t) and film pressure (F) were measured at each film area.

During the initial aging period, the bubbles were stabilized by soluble and insoluble surface-active material, which had been scavenged by the bubble on its rise to the surface. This film was adsorbed at the air-water interface around the bubble, thereby stabilizing the bubble film against immediate rupture at the surface. In organically rich seawater, the t values were somewhat greater than those caused by a number of pure insoluble monolayers, described in Garrett (1967). This greater stability may be due to the rapid repair of the protective surface film by the available supply of readily adsorbable soluble organics from the bulk seawater. It should be noted, the bubbles burst instantaneously at the surface of clean distilled water.

Once the surface had aged, and the adsorbed surface film was compressed, t decreased substantially (Figure 2), and the repeatability of the lifetime measurement increased. As F increased, due to compression of the surface film, the magnitude of t decreased to a few seconds, a result similar to that for the insoluble monolayers. Thus, although natural surface-active
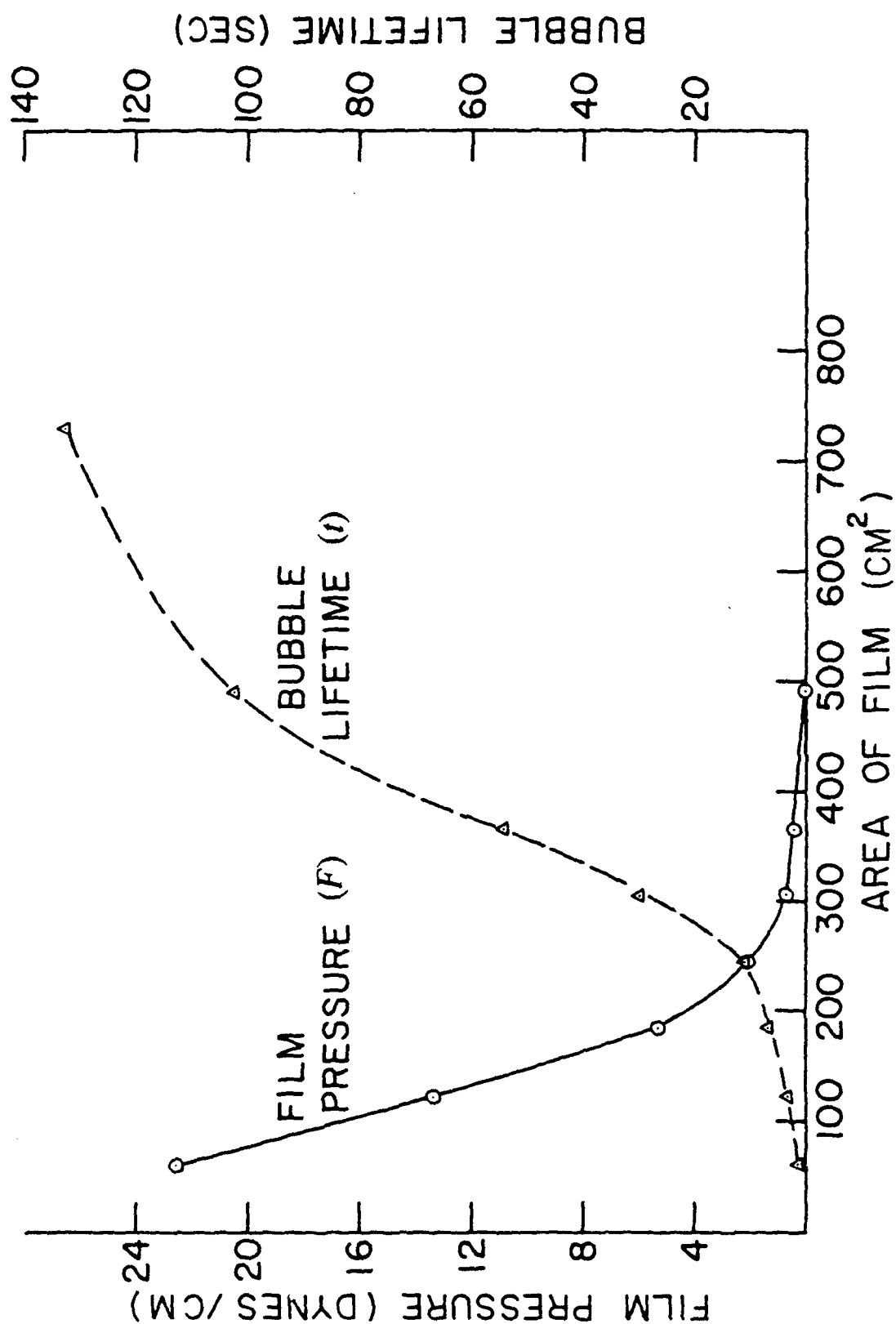
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Figure 2. Bubble Lifetime (dashed line) and Film Pressure (solid line) vs. Area of Sea-Surface Film

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material is present on the inner air bubble surface, the compressed monolayer at the air-sea interface is the controlling factor in determining bubble lifetime.

In the ensuing discussion of monolayer-produced bubble-stability mechanisms, reference will be made to Figure 3, a schematic diagram of a single air bubble at a monolayer-covered surface. Processes important to the stability of the bubble are indicated on the schematic. The infinitesimal ($-\delta F$) represents a temporary decrease in film pressure created by a local increase in surface area as the bubble protrudes above the plane of the water surface. If the monolayer is soluble, the shortest path to the inner bubble-water interface is at the thinnest portion of the bubble film (solubility path).

The bubble-stability maximum, and its subsequent decrease, with increasing film pressure, can be explained in terms of two opposing surface effects. For the case of an insoluble film on distilled water, as film-forming molecules are added to the surface, bubble lifetime values are zero until there is a surface tension gradient of sufficient magnitude to drive surface film molecules into the expanded surface area, created by the protruding bubble crown. In this region, molecules are further apart and the surface tension is greater. The surface tension gradient flow is in opposition to the drainage of water in the underlying bubble lamella. At low film pressures, this flow is unimpeded, and the bubble is stabilized against rupture.

The decrease in lifetime, which occurs at greater film pressures, can be attributed to an increase in intermolecular forces between molecules in the surface film. Molecular interactions increase at higher film pressures as the molecules are forced into closer contact. This effect resists the gradient flow of the surface film into the area of greater surface tension created at the top of the bubble. As cohesive forces between the film molecules increase, changes in tension in the upper bubble surface are not counterbalanced immediately. Thus, the probability of rupture sites increases as the lamella thins, and the bubble is more likely to burst.

The resistance to flow under a surface tension gradient was also demonstrated at high film pressures by another observation. It was necessary to allow up to 30 seconds between measurements to obtain reproducible bubble lifetime values. The waiting period allowed the surface film to return to its equilibrium condition of total coverage after the disruption caused by the previous bubble burst. In most cases, bubble lifetime values, taken within seconds of a previous value, were zero at high film pressure, indicating slow repair of the rigid monolayer in which the molecules are tightly packed.

Although this paper is not concerned with bubble stability *per se*, these bubble lifetime data indicate that at high pressures, natural films resist flow under a surface tension gradient.
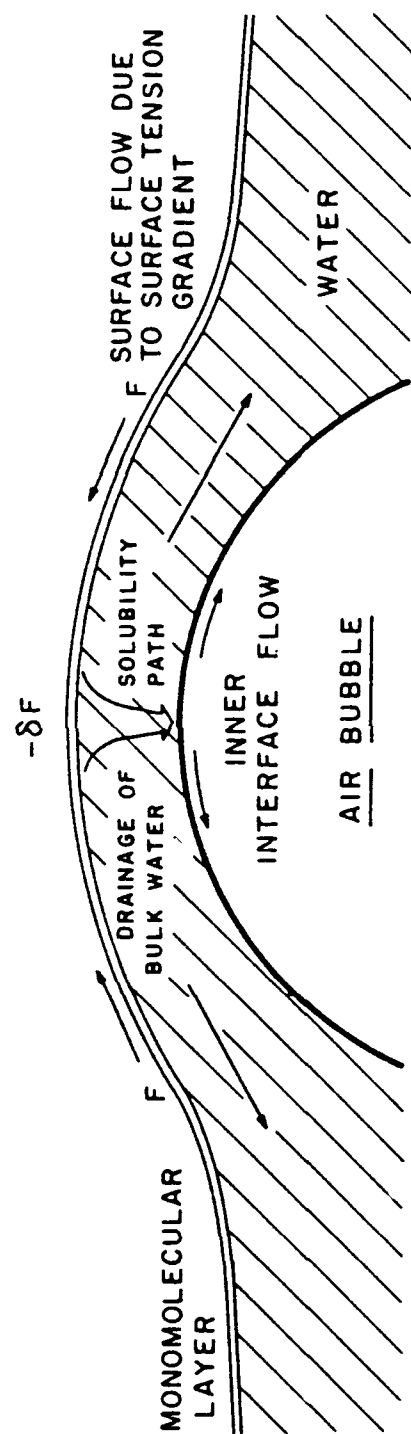
Figure 3. Surface Chemical Factors Affecting the Lifetime of an Air Bubble at a Water Surface

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This information, and the data presented in subsequent sections, may provide an explanation of observed sea surface film persistence under conditions where film-confining forces apparently do not exist.

3.2   Surface Film Modifications Under Dynamic Conditions

On a dynamic sea surface natural films, approximately 3 nanometers in thickness, are subjected to numerous dispersive processes as well as interfacial actions of wind and waves, which modify film chemistry and physics. An adsorbed film is compressed and expanded by wave-induced surface compressions and dilations. During this *working* of the film, less polar and more soluble constituents are excluded and the organic layer becomes enriched in the more strongly adsorbed species. Also during periods of expansion, intermolecular cohesive forces are reduced and more volatile species may evaporate.

Loss of film constituents is demonstrated in Figure 4, a series of repeated, constant-rate compressions of a natural film allowed to adsorb at the surface of a microlayer seawater sample collected with a rotating drum skimmer (Frew, 1990). In this study, a film was allowed to develop for 12 hours, then compressed and expanded 10 times at a constant rate. There was a decrea e of film area for a particular pressure, but the rate of decrease diminished with repeated compr ssions. This result would be expected if most of the soluble species are lost in the first few fi'n compressions. For comparison purposes, curve 12 is an F vs. A plot of the organic film which developed on clean seawater that had been sampled at an average depth of 10 cm from the same sampling site. The slope of the F vs. A curve increases with subsequent compressions, and the filr becomes less expanded in character. In the extended compression (curve 11), the film was driven to 8 percent of its original area, reexpanded and compressed again at the same rate. In this instance, it is likely that the film was compressed past its collapse pressure, at which point portior s of the film crumpled into a three-dimensional matrix, and many of its constituents were unable to readsorb readily at the air-water interface and respread within the time of the expans on.

Hysteresis loops in the F vs. A curves of natural films also provide some insight into film properties under dynamic conditions. Figure 5 depicts two compressions and expansions of a natural film on its seawater substrate. In addition to loss of film constituents, there is a hysteresis in the decay of film pressure at a particular area. This may be due to intermolecular forces which inhibit rapid respreading away from the measurement device, a Wilhelmy plate. It is possible that at very high pressures, or with compressions past the collapse point of the film, the hysteresis might be even more pronounced, and recovery to the original F vs. A curve might take a very long time.
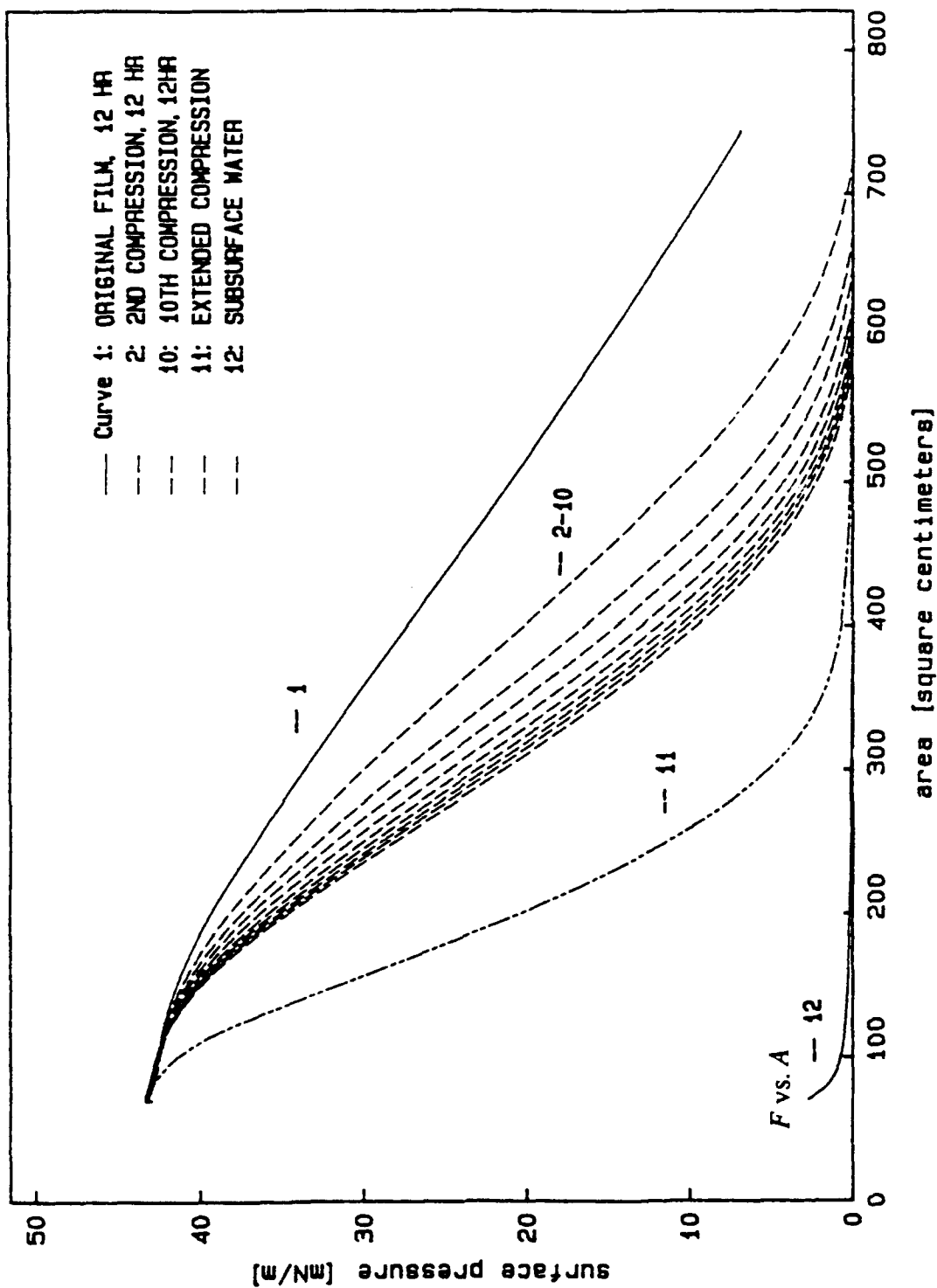
Figure 4. Effect of Repeated Compressions and Expansions on Surface
Pressure vs. Area Curves of a Natural Sea-Surface Film

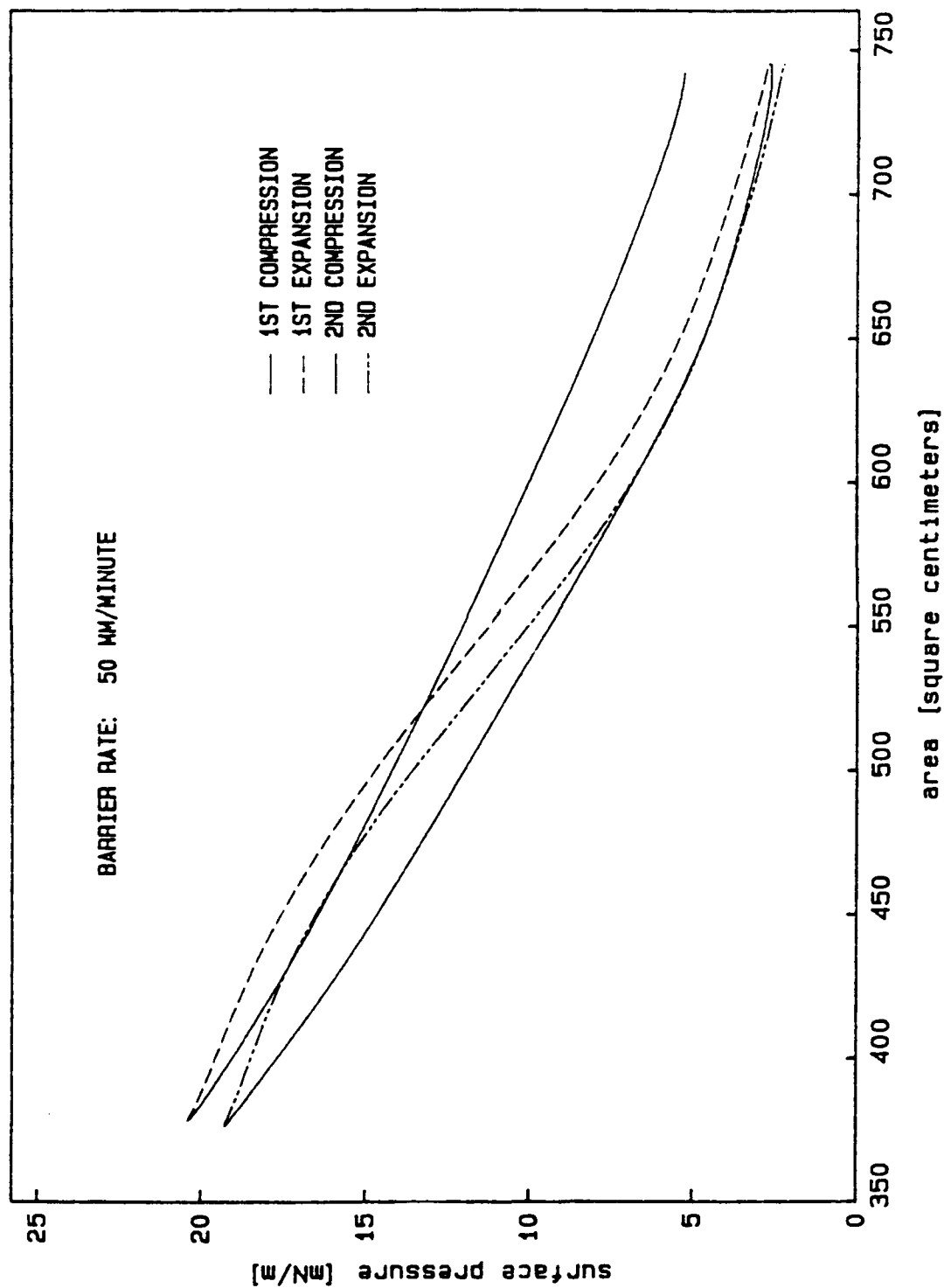MICROLAYER FILM   HYSTERESIS LOOP   2 CYCLES

BARRIER RATE: 50 MM/MINUTE

1ST COMPRESSION
1ST EXPANSION
2ND COMPRESSION
2ND EXPANSION

area [square centimeters]

surface pressure [mN/m]

Figure 5. Hysteresis in Surface Pressure vs. Area Curves
for a Natural Sea-Surface Film

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3.3 Photochemical Effects

Nelson, writing in Katz et al. (1988), considers the scar persistence problem, and suggests the possibility that photocatalyzed polymerization of sea surface film constituents may occur with exposure to sunlight. It is indicated that there is a potential for interfacial polymerization of ethylene or vinyl groups and alkyl alanines into structures that presumably would resist sea surface spreading and account for the observation of persistent films. It is noted that the solubility of solar oxidized films should decrease and that film dispersal would decrease dramatically.

On a somewhat contrasting note, Timmons, (1962), found that the exposure of plankton oil films on a synthetic seawater substrate to artificial sunlight produced expanded films with greater surface compressibilities. Since this report is relatively unknown and difficult to obtain, it is reproduced at the end of this paper as Appendix A. Timmons was a part of the Zisman, Jarvis, and Garrett team which pioneered studies of the chemistry and physics of sea surface films in the 1960s. He found that photocatalyzed oxidation of double bonds in the planktonic oil lipids generated more oxygenated hydrophillic groups that adsorbed at the air-water interface. The films expanded with time of exposure as measured by their specific areas (plotted as square meters per milligram). After extended sunlight exposure, the specific area decreased in one of the experiments, and there was evidence of molecular scission, leading to soluble species of lower molecular weight. The influence of extended photocatalyzed oxidation on films under dynamic stresses was not determined, and should be included in future research into scar persistence.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The larger ships appear to generate turbulent wakes, which are highlighted by surface films ior the longest times late and the greatest distances. These include freighters, tankers, and large naval vessels with considerable momentum, speed, and displacement. It is likely that these ships generate strong convergence zones on either side of the wake, which would produce greater surface strain rates than those generated by smaller vessels. These surface convergences might be sufficiently strong to compress portions of the ambient film beyond its collapse point (see Section 3.2) into a three-dimensional matrix. More soluble and fluid film-forming substances would leave the surface, and the remaining film would resist respreading into clean water. The resistance to spreading is a result of strong intermolecular cohesional forces between close-packed hydrocarbon chains in the film at high pressures. In addition, the collapsed molecular clusters of surface-active material would serve as a reservoir of slow-spreading film-forming

material to maintain a slicked edge band after the ship-generated surface currents subside. This proposition should be examined through experimentation to be outlined later in this section.

The influence of sunlight (actinic effects) on a sea-surface film may result in interfacial polymerization (Nelson, 1988), or the photochemical oxidation and subsequent molecular scission suggested by the experiments of Timmons (1962) on plankton oil films. The latter study may not have exactly duplicated the effects of solar radiation on a natural film, since ambient film contain many organic substances in addition to those in plankton oil. The exact influence of solar radiation on the properties of organic films is not yet clear. It is recommended that this subject be studied, along with highly compressed films in future experimentation.

To search for the causes of surface-film related scar persistence, an experiment plan is proposed that combines the effects of air-sea interfacial dynamics and solar radiation. It includes three principal components: (1) since it is not possible to duplicate the chemistry of the sea surface with a chemical model film, the experiments should be performed on natural films adsorbed at the surface of their seawater substrate. To obtain an enriched quantity of film-forming material, the requisite seawater samples could be collected with a surface sampling device (Garrett and Duce, 1980); (2) An elongated shallow trough should be used to contain the seawater samples. The sides of the trough should be hydrophobic to prevent sample overflow. Motor-driven surface barriers would provide compression and expansion of the film at controlled rates. The film measurement system need not be a commercial hydrophil balance, but similar in its film manipulation and measurement capabilities. The surface tension (film pressure) should be determined continuously by the Wilhelmy Plate or other systems accurate to ± 1 mN per meter. At least two surface tension measurement devices will be required; one in the compression zone and one at the opposite end of the trough, into which a film will be allowed to spread; (3) The *bottom line* measurement should be the rate of spreading of a natural film after:

    (a) a number of compression and expansion cycles,

    (b) repeated extended compressions past the film collapse point, and

    (c) exposure to artificial sunlight by itself and in conjunction with experiments (a) and (b).

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APPENDIX A

Stability of Plankton Oil Films
to Artificial Sunlight

C.O. Timmons

STABILITY OF PLANKTON OIL FILMS
TO ARTIFICIAL SUNLIGHT

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June 13, 1962

STABILITY OF PLANKTON OIL FILMS TO ARTIFICIAL SUNLIGHT

INTRODUCTION

Studies have previously been made of the chemical composition of Calanus (1), an abundant species of zooplankton, and the spreading behavior of its oil extract (plankton oil) at the air/water interface (2). Plankton oil is a highly surface active material which consists primarily of unsaturated C_{16}, C_{18}, C_{20}, and C_{22} acids and their triglycerides. These compounds average more than one double bond per molecule. Since naturally occurring slicks at sea are usually monomolecular in nature and may be composed of this or similar materials, it was of interest to learn how long such films would endure on a calm sea after being generated. Although such a film on the sea would be subjected to various destructive forces other than those of photochemical nature, it was felt that a study of the effect of sunlight on film properties would yield indicative information on film persistence.

The most probable effect of light on a monomolecular film of an unsaturated compound would be to catalyze an oxidation reaction. Oxidation reactions of unsaturated fatty acid monolayers have been studied on dilute aqueous $KMnO_4$ substrates by Hilditch (3) and Gilby and Alexander (4). The reaction proceeds in two distinct stages: the addition of two hydroxyl groups at the double-bond site causing an expansion of the monolayer and the subsequent cleavage of the molecule at this site with the formation of two carboxyl groups. The two resulting molecules would be more water soluble and disappear from the surface film. Mittelmann and Palmer (5) found that the disappearance of an oxidizing triolein monolayer did not follow a simple first-order law and suggested that the product of the first reaction may contain, in addition to the dihydroxy compound, a peroxide which could subsequently polymerize. Hughes and Rideal (6) showed the relation of reaction rate of several unsaturated fatty acids to film pressure. Ease of oxidation is a result of the accessibility of the double bond to the oxidizing agent. At higher film pressures the double bond is removed from the substrate and the reaction rate accordingly decreases.

Although a single double bond absorbs ultraviolet radiation of about 200 mμ, which is well below the lower limit of solar radiation passing through the earth's atmosphere, it is possible that the sunlight reaching the surface of the sea can cause some photochemical reaction. The presence of conjugated double bonds (which are probably present in plankton oil) increases the wavelength at which the molecule absorbs. A conjugated tetraene, for example, absorbs radiation at a slightly longer wavelength than 300 mμ. Further, it has been reported by Mitchell and Rideal (7) that the presence of metallic ions in the substrate can cause some reactions to take place in visible light.

EXPERIMENTAL EQUIPMENT AND MATERIALS

Artificial sources of ultraviolet radiation do not duplicate exactly natural sunlight and they differ greatly in spectral energy distribution among themselves. Hirt and coworkers (8) have recently reported measurements of the spectral energy distribution of many light sources and comparisons with sunlight. They conclude that the xenon arcs gave the best approximation when a suitable short-wavelength filter was used.

A xenon-arc lamp, model 418C-1, obtained from the Hanovia Lamp Division of Engelhard Hanovia, Inc., was used in this work in conjunction with a Pyrex 7740 filter to absorb radiation below about 300 mμ. The spectral distribution of the radiation from the xenon

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arc-filter assembly was measured with a uranyl oxalate actinometer and a Perkin-Elmer spectrophotometer. The radiation intensity was measured with the lamp 20 cm from the actinometer solution. The similarity of this source to sunlight is shown in Fig. 1. All curves except the one shown for the xenon-arc lamp are taken from the data of Hirt. In the following experiments all of the films on water were exposed from a distance of 20 cm to insure an approximation of sunlight.
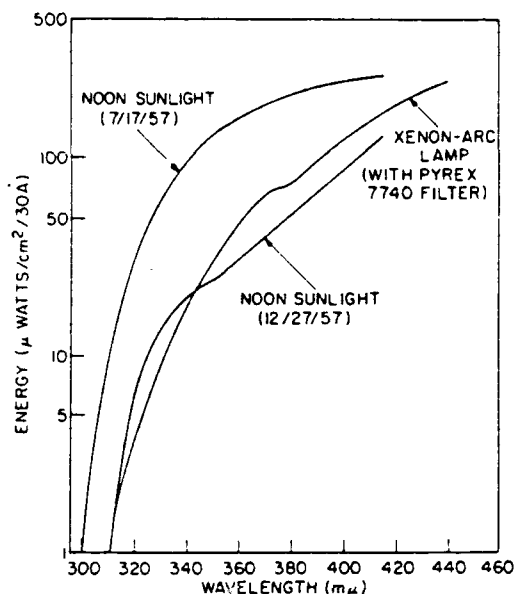

Fig. 1 - Comparison of radiation from xenon-arc lamp with natural sunlight

The apparatus is shown schematically in Fig. 2. The effect of radiation on the plankton oil film was determined by measuring the film pressure vs film area after various exposure times with a Langmuir-Adam type film balance. The film balance consisted of a Pyrex trough (12 cm × 74 cm × 3 mm) with paraffined edges, equipped with a Cenco torsion head (sensitivity of 1.91 degrees per dyne/cm) fitted with a paraffined mica float and polyethylene end loops. As considerable amounts of water evaporated from the trough, a simple constant-levelling device was used to maintain the water level. This consisted of an inverted flask in a reservoir connected to the film balance with a siphon. As the substrate used in this work was synthetic sea water (9), distilled water was used in the leveling device to maintain a constant salt content in the substrate. The composition of the synthetic sea water is given in Table 1.

A Cenco-du Nuoy ring tensiometer, fitted with a platinum ring 4 cm in circumference, was used to measure any surface tension changes occurring on the side of the mica float not covered with the film being studied. Such changes are always possible if any oxidative breakdown of the insoluble monolayer results in the formation of lower molecular weight products which dissolve in the substrate and subsequently readsorb to some extent in the normally clean surface area on the other side of the mica float.

The plankton oil (1) was freshly prepared as before from plankton collections obtained during an oceanographic expedition of May 1960. This oil was dissolved in petroleum ether and spread on the substrate of the balance from a micrometer syringe. Each period of exposure was begun with the film initially at a pressure of less than 0.1 dyne/cm to avoid any variation in reaction rate from differences in pressure or molecular orientation.

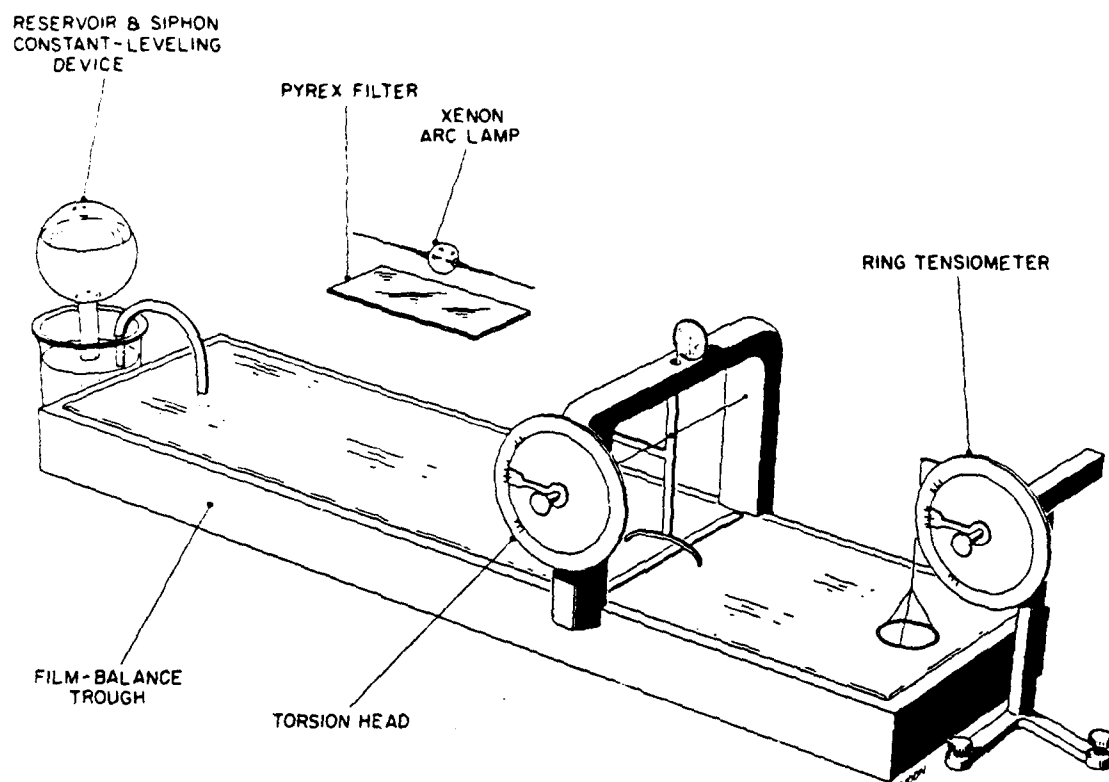All work was performed at a substrate temperature between 23° and 24°C.

Fig. 2 - Prespective drawing of experimental apparatus

Table 1

Salt	Concentration (g/l)
NaCl	24.54
$MgCl_2 \cdot 6H_2O$	11.10
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.69
$NaHCO_3$	0.20
KBr	0.10
H_3BO_3	0.03
$SrCl_2 \cdot 6H_2O$	0.04
NaF	0.003

RESULTS

Figures 3 and 4 show force vs area isotherms for plankton oil monolayers on a synthetic sea water substrate for exposure times up to 19 hours (run A) and 18 hours (run B), respectively. Although the results of both runs were not identical, they agree in many respects. The unexposed plankton oil has a specific area of 1.2 m^2/mg at a film pressure of 2 dynes/cm, and a collapse pressure of 28.5 dynes/cm. In Fig. 3 it is seen that film expansion occurs rapidly during the first 3 hours of exposure and then the rate gradually decreases until after 15 hours a slow contraction commences and the specific area decreases. This is accompanied by increases in collapse pressure to something greater than 40 dynes/cm. Figure 4 is similar to Fig. 3 in showing that the most rapid film expansion occurs during the first 6 hours of exposure followed by a gradual slowing of the rate. A slow expansion also begins again after 12-hour exposure, but in this run no decrease in specific area ever occurs. Collapse pressures here also increase from the original 28.5 dynes/cm to something in the neighborhood of 40 dynes/cm.

Figure 5 is a plot of specific area vs exposure time for the film at a pressure of 2 dynes/cm. This figure clearly points out variations in reaction rate with time. In run A it is again seen that the most rapid expansion occurs during the first 3 hours of exposure followed by a gradual decrease in rate. After 15 hours a slow contraction of the film begins. In run B the most rapid expansion occurs during the first 6 hours of exposure with a subsequent gradual decrease in rate. In this case, however, there is neither a contraction of the film nor a decrease in specific area.
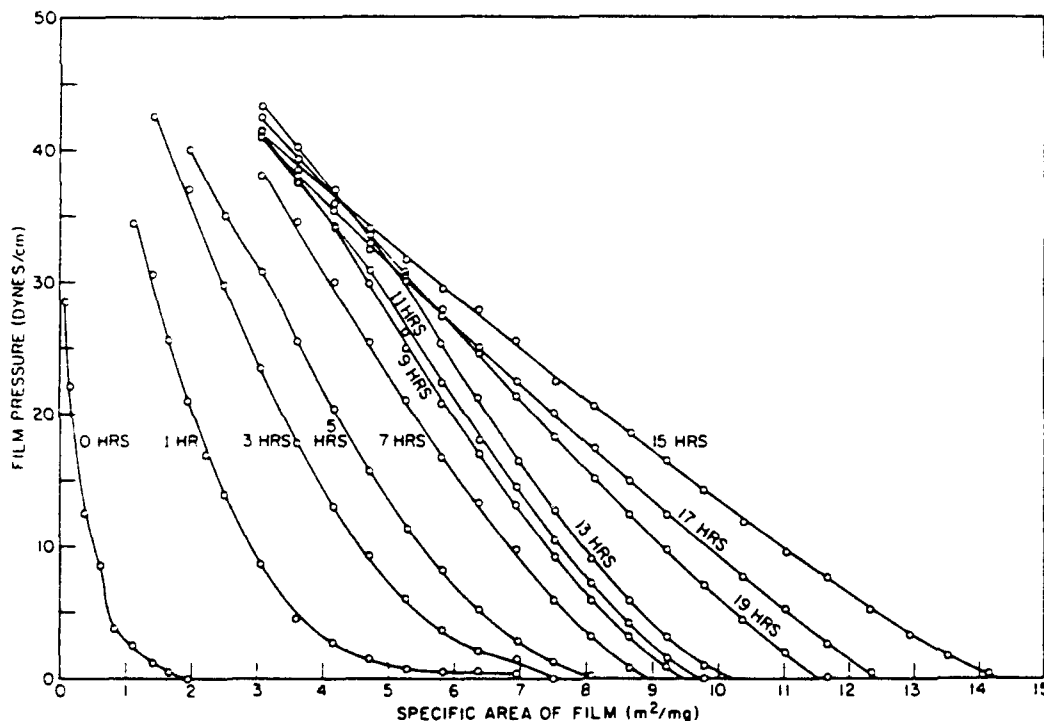

Fig. 3 - Run A, 19-hr exposure of plankton oil
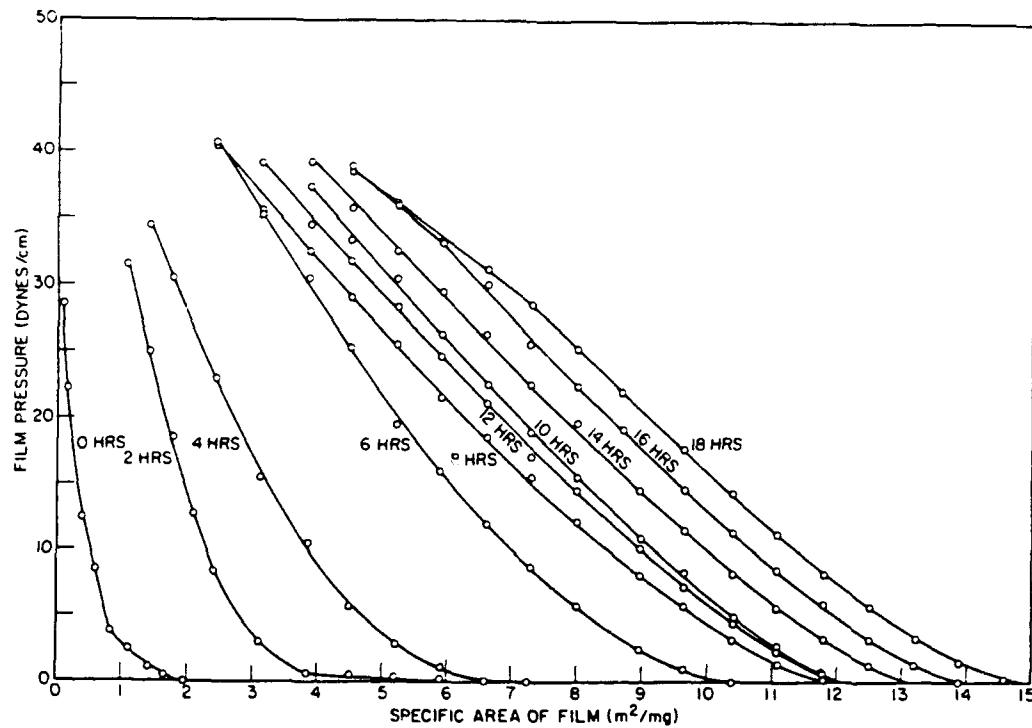on synthetic sea water at 23° -24°C

Fig. 4 - Run B, 18-hr exposure of plankton oil
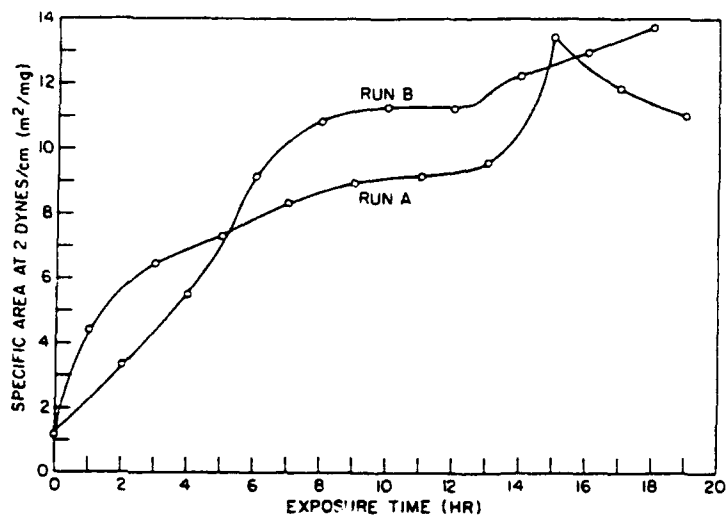on synthetic sea water at 23° -24° C

Fig. 5 - Variation in specific area at 2 dynes/cm
with exposure time

Changes in surface tension occurring in the normally clean area of the aqueous sub-strate on the outside of the mica float are shown in Fig. 6. The curve of run A, represent-ing the 19-hour exposure, rises gradually at first and then more rapidly after about 13 hours. There is only a general, overall rise in the curve of run B, the 18-hour exposure.
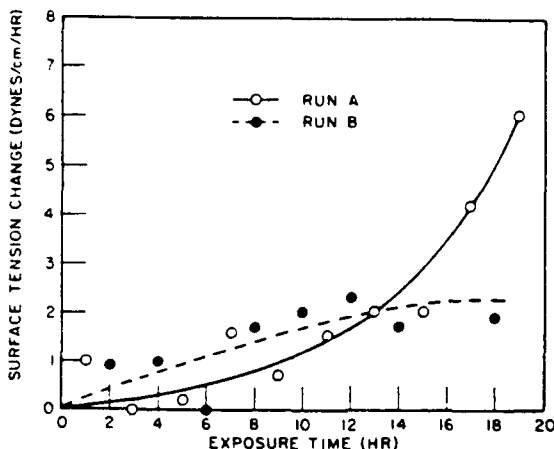

Fig. 6 - Variation in surface tension in area separated from film by mica float

DISCUSSION

The plankton oil film, although initially a readily condensed liquid monolayer, expands rapidly through photochemical reaction to become a highly expanded gaseous monolayer film. This is the result of the oxidizing unsaturated molecules adding additional hydrophilic groups at the double-bond sites, and an increasing proportion of the molecules becoming adsorbed in a nearly horizontal position on the aqueous substrate.

Expansion continues until, as in the case of run A, the monolayer begins to dissolve, as shown by a decrease in the specific area, presumably as a result of further oxidation and possible cleavage of the oxidized molecules. It is believed that the 18-hour exposure in run B was not long enough to show the decrease in specific area. It can be noticed in Fig. 4 that the isotherms for the 16th and 18th hour of exposure are nearly coincidental at high film pressures. This was the same condition achieved before film breakdown occurred in a run A although it occurred in a shorter period of time in that case.

It is significant that in both exposures the coincidence of the force vs area isotherms at high film pressures occurs where the estimated film thickness (assuming the specific gravity of the oil to be 0.9) is about 3 or 4A. Since a hydrocarbon chain in its elongated or normal configuration is approximately the same (2.5A thick), one can only conclude that oxidation has proceeded to the point where each molecule is lying with its principal axis parallel to the air/water interface.

The high collapse pressures of the expanded films in both runs may be explained by considering the probable oxidation products of these long-chain, unsaturated hydrocarbons. Presumably, hydroxyl groups are added at the double-bond site followed by cleavage of the molecule with the formation of two carboxyl groups. Either or both of these oxidation steps would tend to increase collapse pressures, as they are usually increased as the ratio of oxygen to hydrocarbon in a molecule increases.

Variations in surface tension of the water surface separated from the film by the mica float also indicate that the first solubilization of the film and its readsorption in this area

began after 15 hours of exposure in the case of run A. The relatively large decrease in surface tension in this area indicates that the breakdown products are only slightly soluble since very soluble materials must be added to water in high concentrations in order to cause a large decrease in surface tension. The exposure time was not sufficient in run B to show this effect. A "dark" reaction was carried out to insure that the effects observed were photochemical. Runs made in the dark, for periods up to 9 hours, showed negligible changes in film properties. Also the possibility of ozonization of the film, instead of oxidation, was not overlooked. The ozone concentration at the film balance was measured during a typical run by the iodide method and was found to be negligible. Negligible also were any effects of radiation on the paraffin used on the film balance. Using the film balance with a clean water surface, the apparatus was exposed for 15 hours. No contamination of the water surface occurred.

SUMMARY

Plankton oil monolayers spread on synthetic sea water and exposed to radiation approximating sunlight rapidly expand during the first several hours of exposure. This expansion is accompanied by an increase in the collapse pressure. These changes are a result of photochemically catalyzed oxidation occurring at the double bond, giving each molecule an additional oxygen-containing point of attachment to the substrate. One case studied showed film breakdown to begin after a 15-hour exposure time. This was evidenced by a decrease in specific area of the film after this time and by a decrease in the surface tension in the normally clean water area separated from the film by the mica float. The other case showed no evidence of film breakdown after an 18-hour exposure.

It is concluded that plankton oil films do not disappear by photocatalyzed oxidation for periods equivalent to at least two days of sunlight, but they will subsequently dissolve by molecular scission. It is, however, possible that such films would not persist this long on the sea because other destructive forces would be acting upon them.

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